EXHIBIT A

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[Document name] Claims

1. A novel phosphonium borate compound represented by Formula (I):

$$(R^1)(R^2)(R^3)PH\cdot BAr_4 \qquad (I)$$

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^1, R^2 and R^3 may be the same or different from one another;

Ar is an aryl group of 6 to 20 carbon atoms;

R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously and Ar cannot be phenyl group at the same time; and

R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously

and Ar cannot be phenyl group at the same time.

2. The phosphonium borate compound according to claim 1, which is di-tert-butylmethylphosphonium tetraphenylborate.

3. The phosphonium borate compound according to claim 1, which is tri-tert-butylphosphonium tetra-para-tolylborate.

4. The phosphonium borate compound according to claim 1, which is tricyclohexylphosphonium tetra-para-tolylborate.

5. The phosphonium borate compound according to claim 1, which is triisopropylphosphonium tetraphenylborate.

6. A process for producing a novel phosphonium borate compound, which comprises:

reacting a phosphine with HCl to produce a phosphine hydrochloride, the phosphine being represented by Formula (II):

$$(R^1)(R^2)(R^3)P \qquad (II)$$

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a

cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms; and

R^1, R^2 and R^3 may be the same or different from one another;

the phosphine hydrochloride being represented by Formula (III):

$(R^1)(R^2)(R^3)PH \cdot Cl$ (III)

wherein R^1, R^2 and R^3 are as defined in Formula (II); and

reacting the phosphine hydrochloride with a tetraarylborate compound represented by Formula (IV):

$M \cdot BAr_4$ (IV)

wherein M is lithium, sodium, potassium, magnesium halide or calcium halide, and Ar is an aryl group of 6 to 20

carbon atoms;

the phosphonium borate compound being represented by Formula (I):

$(R^1)(R^2)(R^3)PH \cdot BAr_4$ (I)

wherein R^1, R^2 and R^3 are as defined in Formula (II), and Ar is as defined in Formula (IV);

R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously and Ar cannot be phenyl group at the same time; and

R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously and Ar cannot be phenyl group at the same time.

7. A process for producing a novel phosphonium borate compound, which comprises:

reacting a phosphine with H_2SO_4 to produce a phosphine sulfate, the phosphine being represented by Formula (II):

$(R^1)(R^2)(R^3)P$ (II)

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms; and

R^1, R^2 and R^3 may be the same or different from one another;

the phosphine sulfate being represented by Formula (V):

$$[(R^1)(R^2)(R^3)PH]_{(2-n)} \cdot H_nSO_4 \qquad (V)$$

wherein R^1, R^2 and R^3 are as defined in Formula (II), and n is an integer of 0 or 1;

and

reacting the phosphine sulfate with a tetraarylborate compound represented by Formula (IV):

$$M \cdot BAr_4 \qquad (IV)$$

wherein M is lithium, sodium, potassium, magnesium halide or calcium halide, and Ar is an aryl group of 6 to 20 carbon atoms;

the phosphonium borate compound being represented by Formula (I):

$$(R^1)(R^2)(R^3)PH \cdot BAr_4 \qquad (I)$$

wherein R^1, R^2 and R^3 are as defined in Formula (II), and Ar is as defined in Formula (IV);

R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously and Ar cannot be phenyl group at the same time; and

R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously and Ar cannot be phenyl group at the same time.

8. Use of the phosphonium borate compound claimed in any one of claims 1 to 5 in combination with a transition metal, transition metal salt, transition metal oxide or transition metal complex in carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein a transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compound in combination with the transition metal, transition metal salt, transition metal oxide or transition metal complex is used in place of the transition metal complex having a phosphine ligand.

9. The use of the phosphonium borate compound according to claim 8, wherein the transition metal is manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium or platinum.

10. The use of the phosphonium borate compound according to claim 8, wherein the transition metal salt is a

fluoride, chloride, bromide, iodide, sulfate, nitrate, nitrite, carbonate, borate, ammonium salt, sodium salt, potassium salt, acetate, trifluoroacetate, acetylacetone salt, hydride salt, sulfide or cyanide of the transition metal as described in claim 9.

11. The use of the phosphonium borate compound according to claim 8, wherein the transition metal oxide is an oxide of the transition metal as described in claim 9.

12. The use of the phosphonium borate compound according to claim 8, wherein the transition metal complex is a benzonitrile complex, acetonitrile complex, triphenylphosphine complex, ethylene complex, allyl complex, butadiene complex, cyclopentadiene complex, cyclooctadiene complex, cyclooctatetraene complex, carbonyl complex, dibenzylideneacetone complex, amine complex, ethylenediamine complex, pyridine complex or disiloxane complex of the transition metal as described in claim 9.

[Document name] Specification

[Title of the invention] NOVEL PHOSPHONIUM BORATE COMPOUND

[Field of the invention]

[0001]

The present invention relates to a novel phosphonium borate compound, a process for the production thereof, and use of the compound.

[Background of the invention]

[0002]

Transition metal complexes having alkylphosphine compounds as ligands are very important catalysts in carbon-carbon bond forming reactions such as Suzuki-Miyaura reaction, carbon-nitrogen bond forming reactions such as Buchwald-Hartwig amination, and carbon-oxygen bond forming reactions such as ether synthesis (see Nonpatent Document 1). As an example, bis(tri-tert-butylphosphine)palladium (0) is used.

[0003]

Many of the transition metal complexes having alkylphosphine ligands are very expensive, and the industrial availability thereof is low. Further, synthesis of the transition metal complexes having alkylphosphine ligands is difficult because the raw-material alkylphosphine compounds are generally extremely susceptible to air oxidation and

possess combustibility.

[0004]

For such reasons, the alkylphosphine compounds are used together with transition metals, salts thereof, oxides thereof or complexes thereof in the reaction system, in place of the isolated transition metal complexes having alkylphosphine ligands (see Nonpatent Documents 1 and 2). For example, di-tert-butylmethylphosphine, tri-tert-butylphosphine or tricyclohexylphosphine is used together with palladium (II) acetate or tris(dibenzylideneacetone)dipalladium (0) in the reaction system.

[0005]

However, many of the alkylphosphine compounds are extremely susceptible to air oxidation and possess combustibility, and therefore are difficult to handle.

[0006]

To improve the susceptibility to air oxidation, alkylphosphonium tetrafluoroborates, quaternary salts of alkylphosphines and boron compounds, have been studied. Examples of the alkylphosphonium tetrafluoroborates include:

(1) tricyclohexylphosphonium tetrafluoroborate (see Nonpatent Document 3);

(2) di-tert-butylmethylphosphonium tetrafluoroborate (see Nonpatent Document 2); and

(3) tri-tert-butylphosphonium tetrafluoroborate (see Nonpatent Document 3).

These compounds are produced from alkylphosphine compounds and fluoroboric acid (see Nonpatent Document 4).

[0007]

As known in the art, the above compounds are used together with transition metals, salts thereof, oxides thereof or complexes thereof in the carbon-carbon bond forming reactions such as Suzuki-Miyaura reaction (see Nonpatent Documents 2 and 4). For example, di-tert-butylmethylphosphonium tetrafluoroborate or tri-tert-butylphosphonium tetrafluoroborate is used together with palladium (II) acetate, tris(dibenzylideneacetone)dipalladium (0) or bis(benzonitrile)dichloropalladium (II) in the reaction system.

[0008]

Fluoroboric acid used as raw material in the production of the compounds (1) to (3) are corrosive and penetrate into the skin upon contact, and must be handled carefully. Furthermore, fluoroboric acid has acidity to corrode production utility made of stainless steel, and when hydrofluoric acid is liberated, it will corrode production utility made of glass. Therefore, the actual use of the above compounds in the production causes problems.

[0009]

Alkylphosphonium tetraarylborate compounds are also developed, and the following compounds are known:

(4) triethylphosphonium tetraphenylborate (see Patent Document 1);

(5) tri-n-butylphosphonium tetraphenylborate (see Patent Document 1 and Nonpatent Document 5);

(6) tricyclohexylphosphonium tetraphenylborate (see Nonpatent Documents 3 and 6); and

(7) tri-tert-butylphosphonium tetraphenylborate (see Nonpatent Documents 3 and 6).

[0010]

Nonpatent Documents 3, 5 and 6 describe the production of the alkylphosphonium tetraarylborate compounds. Specifically, the documents describe the following production processes (8) to (10).

(8) Tricyclohexylphosphine is reacted with fluoroboric acid to synthesize tricyclohexylphosphonium tetrafluoroborate, which is reacted with sodium tetraphenylborate to produce tricyclohexylphosphonium tetraphenylborate (75% yield). A similar process is described in which tri-tert-butylphosphine is used as starting material to produce tri-tert-butylphosphonium tetraphenylborate (71% yield) (see Nonpatent Document 3).

(9) Tri-tert-butylphosphine is reacted with 1,1,1,3,3,3-hexafluoro-2-propanol and with sodium tetraphenylborate to produce tri-tert-butylphosphonium tetraphenylborate (77% yield). A similar process is described in which tricyclohexylphosphine is used as starting material to produce tricyclohexylphosphonium tetraphenylborate (77% yield) (see Nonpatent Document 6).

(10) Tri-n-butylphosphine is reacted with hydrochloric acid in the presence of sodium tetraphenylborate to produce tri-n-butylphosphonium tetraphenylborate (53% yield) (see Nonpatent Document 5).

The four compounds (4) to (7) are the only compounds known as the alkylphosphonium tetraarylborate compounds, and the three processes (8) to (10) are the only known processes for producing them.

[0011]

The processes (8) (Nonpatent Document 3) use fluoroboric acid and consequently have handling problems and problems of corrosion of production facility, and are not suited for industrial production.

[0012]

The processes (9) (Nonpatent Document 6) use 1,1,1,3,3,3-hexafluoro-2-propanol which is expensive, and are not suited for industrial production. More inexpensive

processes are desirable.

[0013]

In the process (10) (Nonpatent Document 5) in which tri-n-butylphosphine is reacted with hydrochloric acid in the presence of sodium tetraphenylborate, the yield of tri-n-butylphosphonium tetraphenylborate is low (53% in terms of tri-n-butylphosphine). The reason for the low yield is not clear but is probably that a side reaction takes place between the reaction product of sodium tetraphenylborate with hydrochloric acid, and tri-n-butylphosphine.

[0014]

The documents recited above do not describe that the carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein the transition metal complexes having phosphine ligands produce catalytic effects, may be catalyzed by phosphonium tetraarylborate compounds together with transition metals, salts thereof, oxides thereof or complexes thereof in place of the transition metal complexes having phosphine ligands.

[0015]

Thus, there is a need for the development of alkylphosphine derivatives that are producible without special reaction equipment and by simple operations, and have

good handling properties.

Patent Document 1: JP-A-S62-149721 (pp. 2 and 3)

Nonpatent Document 1: Journal of American Chemical Society (U.S.A.) (2000, vol. 122, No. 17, pp. 4020-4028)

Nonpatent Document 2: Journal of American Chemical Society (U.S.A.) (2002, vol. 124, No. 46, pp. 13662-13663)

Nonpatent Document 3: Journal of American Chemical Society (U.S.A.) (1991, vol. 113, No. 3, pp. 875-883)

Nonpatent Document 4: Organic Letters (U.S.A.) (2001, vol. 3, No. 26, pp. 4295-4298)

Nonpatent Document 5: Organometallics (U.S.A.) (1999, vol. 18, No. 20, pp. 3981-3990)

Nonpatent Document 6: Journal of American Chemical Society (U.S.A.) (1997, vol. 119, No. 16, pp. 3716-3731)

[Disclosure of the invention]

[Problems to be solved by the invention]

[0016]

It is an object of the present invention to provide a novel phosphonium borate compound that is easily handled. It is another object of the invention to provide a novel process whereby a phosphonium borate compound is produced safely on an industrial scale, by simple reaction operations and in a high yield. It is a further object of the invention to provide a novel use of the phosphonium borate compound in combination

with a transition metal, salt thereof, oxide thereof or complex thereof in the carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein a transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compound in combination with the transition metal, salt thereof, oxide thereof or complex thereof is used in place of the transition metal complex having a phosphine ligand.

[Means for solving the problems]

[0017]

The present inventors studied diligently to achieve the above objects, and they have found that a novel phosphonium borate compound can be produced safely, by simple reaction operations, and in a high yield by reacting a phosphine (II) with hydrochloric or sulfuric acid, and reacting the reaction product with a tetraarylborate compound (IV). The inventors have also found the novel phosphonium borate compound is highly resistant to oxidation as compared to alkylphosphine compounds. It has been also found that the phosphonium borate compound in combination with a transition metal, salt thereof, oxide thereof or complex thereof can be used in the carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein a

transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compound in combination with the transition metal, salt thereof, oxide thereof or complex thereof is used in place of the transition metal complex having a phosphine ligand.

[0018]

In a first aspect of the present invention, there is provided a novel phosphonium borate compound represented by Formula (I):

$(R^1)(R^2)(R^3)PH \cdot BAr_4$ (I)

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon

atoms, or an allyl group of 3 to 20 carbon atoms;

R^1, R^2 and R^3 may be the same or different from one another;

Ar is an aryl group of 6 to 20 carbon atoms;

[0019]

R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously and Ar cannot be phenyl group at the same time; and

R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously and Ar cannot be phenyl group at the same time.

[0020]

In a second aspect of the present invention, there is provided a process for producing a novel phosphonium borate compound represented by Formula (I), which comprises:

reacting a phosphine with HCl to produce a phosphine hydrochloride, the phosphine being represented by Formula (II):

$$(R^1)(R^2)(R^3)P \qquad (II)$$

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms; and

R^1, R^2 and R^3 may be the same or different from one another;

the phosphine hydrochloride being represented by Formula (III):

$(R^1)(R^2)(R^3)PH \cdot Cl$ (III)

wherein R^1, R^2 and R^3 are as defined in Formula (II); and

reacting the phosphine hydrochloride with a tetraarylborate compound represented by Formula (IV):

$M \cdot BAr_4$ (IV)

wherein M is lithium, sodium, potassium, magnesium halide or calcium halide, and Ar is an aryl group of 6 to 20 carbon atoms.

[0021]

In a third aspect of the present invention, there is provided a process for producing a novel phosphonium borate compound represented by Formula (I), which comprises:

reacting a phosphine with H_2SO_4 to produce a phosphine

sulfate, the phosphine being represented by Formula (II):

$(R^1)(R^2)(R^3)P$ (II)

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms; and

R^1, R^2 and R^3 may be the same or different from one another;

the phosphine sulfate being represented by Formula (V):

$[(R^1)(R^2)(R^3)PH]_{(2-n)} \cdot H_nSO_4$ (V)

wherein R^1, R^2 and R^3 are as defined in Formula (II), and n is an integer of 0 or 1;

and

reacting the phosphine sulfate with a tetraarylborate

compound represented by Formula (IV):

$M \cdot BAr_4$ (IV)

wherein M is lithium, sodium, potassium, magnesium halide or calcium halide, and Ar is an aryl group of 6 to 20 carbon atoms.

[0022]

In a fourth aspect of the present invention, there is provided use of the novel phosphonium borate compound produced as described above in combination with a transition metal, transition metal salt, transition metal oxide or transition metal complex in carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein a transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compound in combination with the transition metal, transition metal salt, transition metal oxide or transition metal complex is used in place of the transition metal complex having a phosphine ligand.

[Preferred embodiments of the invention]

[0023]

The novel phosphonium borate compound, process for the production thereof, and use of the compound will be described in detail hereinbelow.

[0024]

[Phosphonium borate compound]

The novel phosphonium borate compound is represented by Formula (I):

$(R^1)(R^2)(R^3)PH \cdot BAr_4$ (I)

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^1, R^2 and R^3 may be the same or different from one another;

Ar is an aryl group of 6 to 20 carbon atoms;

[0025]

R^1, R^2 and R^3 are not tert-butyl groups simultaneously and Ar is not phenyl group at the same time; and

R^1, R^2 and R^3 are not cyclohexyl groups simultaneously and Ar is not phenyl group at the same time.

[0026]

$\underline{R^1}$

In Formula (I), R^1 is as described below.

[0027]

R^1 may be a secondary alkyl group, desirably a secondary alkyl group having 3 to 20, preferably 3 to 11 carbon atoms. The secondary alkyl groups include isopropyl, sec-butyl, 2-pentyl, 3-pentyl, 2-hexyl and 3-hexyl.

[0028]

R^1 may be a tertiary alkyl group, desirably a tertiary alkyl group having 4 to 20, preferably 4 to 11 carbon atoms. The tertiary alkyl groups include tert-butyl, tert-amyl, 1,1-dimethylbutyl, 3-methyl-3-pentyl and 1,1,2-trimethylpropyl.

[0029]

R^1 may be a cycloalkyl group, desirably a cycloalkyl group having 3 to 20, preferably 3 to 11 carbon atoms. The cycloalkyl groups include cyclopropyl, cyclopentyl, cyclohexyl, 1-methylcyclohexyl, 2-methylcyclohexyl, 1-adamantyl, 2-methyl-1-adamantyl, 2-adamantyl, 1-methyl-2-adamantyl and 2-methyl-2-adamantyl. R^1 is not limited to the groups described above.

[0030]

<u>R^2</u>

In Formula (I), R^2 is as described below.

[0031]

R^2 may be a primary alkyl group, desirably a primary alkyl group having 1 to 20, preferably 1 to 8 carbon atoms. The primary alkyl groups include methyl, ethyl, n-propyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, 2-methyl-1-pentyl, 2,2-diethyl-1-ethyl, n-heptyl and n-octyl.

[0032]

R^2 may be a secondary alkyl group, desirably a secondary alkyl group having 3 to 20, preferably 3 to 11 carbon atoms. The secondary alkyl groups include isopropyl, sec-butyl, 2-pentyl, 3-pentyl, 2-hexyl and 3-hexyl.

[0033]

R^2 may be a tertiary alkyl group, desirably a tertiary alkyl group having 4 to 20, preferably 4 to 11 carbon atoms. The tertiary alkyl groups include tert-butyl, tert-amyl, 1,1-dimethylbutyl, 3-methyl-3-pentyl and 1,1,2-trimethylpropyl.

[0034]

R^2 may be a cycloalkyl group, desirably a cycloalkyl group having 3 to 20, preferably 3 to 11 carbon atoms. The cycloalkyl groups include cyclopropyl, cyclopentyl, cyclohexyl,

1-methylcyclohexyl, 2-methylcyclohexyl, 1-adamantyl, 2-methyl-1-adamantyl, 2-adamantyl, 1-methyl-2-adamantyl and 2-methyl-2-adamantyl.

[0035]

R^2 may be an aralkyl group, desirably an aralkyl group having 7 to 20, preferably 7 to 12 carbon atoms. The aralkyl groups include benzyl, 1-phenylethyl, 2-phenylethyl, 2-ethenylbenzyl, 3-ethenylbenzyl, 4-ethenylbenzyl, 4-(2-ethenylphenyl)butyl, 4-(3-ethenylphenyl)butyl and 4-(4-ethenylphenyl)butyl.

[0036]

R^2 may desirably be an allyl group having 3 to 20, preferably 3 to 8 carbon atoms. The allyl groups include allyl and 2-octenyl. R^2 is not limited to the groups described above.

[0037]

<u>R^3</u>

In Formula (I), R^3 is as described below.

[0038]

R^3 may be a primary alkyl group, desirably a primary alkyl group having 1 to 20, preferably 1 to 8 carbon atoms. The primary alkyl groups include methyl, ethyl, n-propyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, 2-methyl-1-pentyl, 2,2-diethyl-1-ethyl, n-heptyl and n-octyl.

[0039]

R^3 may be a secondary alkyl group, desirably a secondary alkyl group having 3 to 20, preferably 3 to 11 carbon atoms. The secondary alkyl groups include isopropyl, sec-butyl, 2-pentyl, 3-pentyl, 2-hexyl and 3-hexyl.

[0040]

R^3 may be a tertiary alkyl group, desirably a tertiary alkyl group having 4 to 20, preferably 4 to 11 carbon atoms. The tertiary alkyl groups include tert-butyl, tert-amyl, 1,1-dimethylbutyl, 3-methyl-3-pentyl and 1,1,2-trimethylpropyl.

[0041]

R^3 may be a cycloalkyl group, desirably a cycloalkyl group having 3 to 20, preferably 3 to 11 carbon atoms. The cycloalkyl groups include cyclopropyl, cyclopentyl, cyclohexyl, 1-methylcyclohexyl, 2-methylcyclohexyl, 1-adamantyl, 2-methyl-1-adamantyl, 2-adamantyl, 1-methyl-2-adamantyl and 2-methyl-2-adamantyl.

[0042]

R^3 may be an aryl group, desirably an aryl group having 6 to 30, preferably 6 to 22 carbon atoms. The aryl groups include phenyl, ortho-tolyl, meta-tolyl, para-tolyl, 2,3-xylyl, 2,4-xylyl, 2,5-xylyl, 2,6-xylyl, 3,4-xylyl, 3,5-xylyl, mesityl, 2-tert-butylphenyl, 3-tert-butylphenyl, 4-tert-butylphenyl, 2-ethenylphenyl, 3-ethenylphenyl,

4-ethenylphenyl, 2-biphenylyl, 3-biphenylyl, 4-biphenylyl, 1-naphthyl, 2-naphthyl, 1,1′-binaphthalene-2-yl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-tert-butoxyphenyl, 3-tert-butoxyphenyl, 4-tert-butoxyphenyl, 2-dimethylaminophenyl, 3-dimethylaminophenyl, 4-dimethylaminophenyl, 2′-dimethylamino-2-biphenylyl, 8-dimethylamino-1-naphthyl and 2′-dimethylamino-1,1′-binaphthalene-2-yl.

[0043]

R^3 may be an aralkyl group, desirably an aralkyl group having 7 to 20, preferably 7 to 12 carbon atoms. The aralkyl groups include benzyl, 1-phenylethyl, 2-phenylethyl, 2-ethenylbenzyl, 3-ethenylbenzyl, 4-ethenylbenzyl, 4-(2-ethenylphenyl)butyl, 4-(3-ethenylphenyl)butyl and 4-(4-ethenylphenyl)butyl.

[0044]

R^3 may be an alkenyl group, desirably an alkenyl group having 2 to 20, preferably 2 to 8 carbon atoms. The alkenyl groups include vinyl, methallyl and 1-octenyl.

[0045]

R^3 may be an alkynyl group, desirably an alkynyl group having 2 to 20, preferably 2 to 8 carbon atoms. The alkynyl groups include ethynyl, 1-propynyl and 1-octynyl.

[0046]

R^3 may desirably be an allyl group having 3 to 20, preferably 3 to 8 carbon atoms. The allyl groups include allyl and 2-octenyl. R^3 is not limited to the groups described above.

[0047]

As long as R^1, R^2 and R^3 are selected from the above groups, they may have an arbitrary combination in terms of numbers.

[0048]

Ar

In Formula (I), Ar is desirably an aryl group of 6 to 20, preferably 6 to 10 carbon atoms.

[0049]

The aryl groups include phenyl, ortho-tolyl, meta-tolyl, para-tolyl, 2,3-xylyl, 2,4-xylyl, 2,5-xylyl, 2,6-xylyl, 3,4-xylyl, 3,5-xylyl, mesityl, 2-tert-butylphenyl, 3-tert-butylphenyl, 4-tert-butylphenyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-tert-butoxyphenyl, 3-tert-butoxyphenyl and 4-tert-butoxyphenyl. Ar is not limited to the groups described above.

[0050]

In Formula (I), R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously and Ar cannot be phenyl group at the same time, and R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously and Ar cannot be phenyl group at the same time.

[0051]

The novel phosphonium borate compound preferably has Formula (I) given below for the reason that the raw material phosphine (II) and tetraarylborate compound (IV) can be synthesized easily by known methods:

$$(R^1)(R^2)(R^3)PH\cdot BAr_4 \qquad (I)$$

wherein R^1 is a secondary alkyl group of 3 to 6 carbon atoms, a tertiary alkyl group of 4 to 8 carbon atoms, or a cycloalkyl group of 3 to 8 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 8 carbon atoms, a secondary alkyl group of 3 to 6 carbon atoms, a tertiary alkyl group of 4 to 8 carbon atoms, a cycloalkyl group of 3 to 8 carbon atoms, an aralkyl group of 7 to 9 carbon atoms, or an allyl group of 3 to 4 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 8 carbon atoms, a secondary alkyl group of 3 to 6 carbon atoms, a tertiary alkyl group of 4 to 8 carbon atoms, a cycloalkyl group of 3 to 8 carbon atoms, an aryl group of 6 to 15 carbon atoms, an aralkyl group of 7 to 9 carbon atoms, an alkenyl group of 2 to 4 carbon atoms, an alkynyl group of 2 to 4 carbon atoms, or an allyl group of 3 to 4 carbon atoms;

R^1, R^2 and R^3 may be the same or different from one another;

Ar is an aryl group of 6 to 10 carbon atoms;

[0052]

R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously

and Ar cannot be phenyl group at the same time; and

R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously and Ar cannot be phenyl group at the same time.

[0053]

Specific examples of the novel phosphonium borate compounds (I) represented by Formula (I) are shown in Tables 11 to 18 which will be presented later.

[0054]

Of the phosphonium borate compounds (I), preferred are:

(1) di-tert-butylmethylphosphonium tetraphenylborate,

(2) di-tert-butylmethylphosphonium tetra-para-tolylborate,

(3) tri-tert-butylphosphonium tetra-para-tolylborate,

(4) di-tert-butylethylphosphonium tetraphenylborate,

(5) n-butyl-di-tert-butylphosphonium tetraphenylborate,

(6) sec-butyl-di-tert-butylphosphonium tetraphenylborate,

(7) cyclohexyl-di-tert-butylphosphonium tetraphenylborate,

(8) di-tert-butyl-n-octylphosphonium tetraphenylborate,

(9) di-tert-butylphenylphosphonium tetraphenylborate,

(10) 2-biphenylyl-di-tert-butylphosphine tetraphenylborate,

(11) di-tert-butyl-1-naphthylphosphonium tetraphenylborate,

(12) benzyl-di-tert-butylphosphonium tetraphenylborate,

(13) di-tert-butyl(4-ethenylbenzyl)phosphonium tetraphenylborate,

(14) di-tert-butylvinylphosphonium tetraphenylborate,

(15) allyl-di-tert-butylphosphonium tetraphenylborate,

(16) tricyclohexylphosphonium tetra-para-tolylborate and

(17) triisopropylphosphonium tetraphenylborate.

Of these, the compounds (1), (3), (16) and (17) are more preferable.

[0055]

The phosphonium borate compounds (I) are particularly useful in combination with a transition metal, salt thereof, oxide thereof or complex thereof in the carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein a transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compounds in combination with the transition metal, salt thereof, oxide thereof or complex thereof are used in place of the transition metal complex having a phosphine ligand.

[0056]

The processes for producing phosphonium borate compounds (I) will be described below.

[0057]

[Processes for producing phosphonium borate compounds]

The first process for producing a phosphonium borate compound (I) includes:

a 1st step in which the phosphine (II) is reacted with

HCl to give the phosphine hydrochloride (III); and

a 2nd step in which the compound (III) is reacted with the tetraarylborate compound (IV) to produce the phosphonium borate compound (I), as illustrated in the reaction formula below:

[0058]

[Chem. 1]

$$\underset{\text{(II)}}{(R^1)(R^2)(R^3)P} \xrightarrow{\text{HCl}} \underset{\text{(III)}}{(R^1)(R^2)(R^3)PH\cdot Cl} \xrightarrow{\text{M}\cdot\text{BAr}_4\ \text{(IV)}} \underset{\text{(I)}}{(R^1)(R^2)(R^3)PH\cdot BAr_4}$$

[0059]

The second process for producing a phosphonium borate compound (I) includes:

a 1′st step in which the phosphine (II) is reacted with H_2SO_4 to give the phosphine sulfate (V); and

a 2′nd step in which the compound (V) is reacted with the tetraarylborate compound (IV) to produce the phosphonium borate compound (I), as illustrated in the reaction formula below:

[0060]

[Chem. 2]

$$(R^1)(R^2)(R^3)P \xrightarrow{H_2SO_4} [(R^1)(R^2)(R^3)PH]_{2-n} \cdot HnSO_4$$

(II) (V)

$$\xrightarrow{M \cdot BAr_4\ (IV)} (R^1)(R^2)(R^3)PH \cdot BAr_4$$

(I)

[0061]

The first and second production processes can produce the phosphonium borate compound (I) in a high yield. The reason for this effect is not clear, but is probably that a side reaction that takes place when the compound (II), HCl or H_2SO_4, and the compound (IV) are added at the same time can be substantially avoided.

[0062]

The processes for producing the phosphonium borate compounds (I) will be described in detail below. The first process will be discussed first.

[0063]

<First production process>

[1st step]

In the 1st step, a phosphine (II) and HCl are reacted under predetermined conditions.

[0064]

These components will be described below.

[0065]

The phosphine (II) used as a raw material in the production process is represented by Formula (II):

$(R^1)(R^2)(R^3)P$ (II)

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms; and

R^1, R^2 and R^3 may be the same or different from one another.

[0066]

Specific examples of the phosphines (II) are shown in Tables 1 to 4 which will be presented later.

[0067]

Specifically, preferred phosphines (II) include

di-tert-butylmethylphosphine, tri-tert-butylphosphine, di-tert-butylethylphosphine, n-butyl-di-tert-butylphosphine, sec-butyl-di-tert-butylphosphine, cyclohexyl-di-tert-butylphosphine, di-tert-butyl-n-octylphosphine, di-tert-butylphenylphosphine, 2-biphenylyl-di-tert-butylphosphine, di-tert-butyl-1-naphthylphosphine, benzyl-di-tert-butylphosphine, di-tert-butyl(4-ethenylbenzyl)phosphine, di-tert-butylvinylphosphine, allyl-di-tert-butylphosphine, tricyclohexylphosphine and triisopropylphosphine. Di-tert-butylmethylphosphine, tri-tert-butylphosphine, tricyclohexylphosphine and triisopropylphosphine are more preferable. These phosphines (II) are preferable because of easy availability of raw materials.

[0068]

The phosphine compounds of Formula (II) may be produced by or according to known methods.

[0069]

Examples of such methods include, but are not limited to, reaction of phosphinas halides and organo Grignard reagents, reaction of phosphinas halides and organolithium

reagents, and reaction of phosphines and olefins. The phosphines (II) synthesized by the above reactions may be purified prior to use, or may be used without purification.

[0070]

The phosphines (II) may be used in an undiluted form, or may be diluted with a solvent. Herein, the diluting solvents include solvents contained in the unpurified phosphines (II). The unpurified phosphines (II) may be further diluted with a solvent.

[0071]

The solvents are not particularly limited as long as they can dissolve reaction substrates and are inert to the reaction substrates. Examples thereof include water; alcohol solvents such as methanol, ethanol and octanol; aliphatic hydrocarbon solvents such as hexane, heptane and isooctane; aromatic hydrocarbon solvents such as benzene, toluene and xylene; ether solvents such as tetrahydrofuran and dibutyl ether; halogenated hydrocarbon solvents such as chloroform and tetrachloromethane; dimethylsulfoxide and dimethylformamide. The solvents may be used singly or in combination of two or more kinds.

[0072]

HCl used in the production process may be hydrochloric acid or hydrogen chloride gas. The HCl concentration in

hydrochloric acid is not particularly limited, and is desirably in the range of 0.1 to 37% by weight, preferably 10 to 37% by weight.

[0073]

The 1st step involving the above raw materials is performed in a reactor purged with an inert gas such as nitrogen or argon. The addition sequence of the raw materials is not particularly limited. For example, HCl may be added to the phosphine (II), or the phosphine (II) may be added to HCl. When HCl is hydrochloric acid, the addition method is not particularly limited, and it may be added all at once or may be added dropwise intermittently or continuously. The hydrogen chloride gas may be easily added by being blown into the phosphine (II).

[0074]

In the 1st step, the desirable HCl requirement, desirable temperature for smooth reaction, and desirable time to complete the reaction vary depending on the type of the phosphine (II) used, and are selected appropriately.

[0075]

The HCl amount varies depending on the type of the phosphine (II), and is desirably in the range of 0.5 to 5 mol, preferably 0.8 to 1.6 mol per mol of phosphine. The HCl amount in this range enables the production of the phosphonium borate

compound (I) in a high yield.

[0076]

The reaction of HCl is desirably carried out while the solution is at −20 to 150°C, preferably 0 to 80°C and is continuously stirred for up to 24 hours, preferably 30 minutes to 5 hours at the temperature. The reaction under these conditions enables the production of the phosphonium borate compound (I) in a high yield.

[0077]

The completion of the reaction in the 1st step may be determined by confirming the absence of unreacted phosphine (II). Specifically, the organic phase is analyzed by gas chromatography or the like to determine the phosphine (II) in the organic phase. When the analysis confirms substantial absence of the remaining phosphine (II), the reaction is terminated. When the phosphine is still present in the organic phase, the reaction is preferably continued.

[0078]

The reaction solution takes various forms depending on the solvent used. For example, the solution may contain crystals of phosphine hydrochloride (III) (described later), may be a uniform solution or a suspension, or may be a two-phase system consisting of an aqueous phase and an organic phase. In the case of the two-phase system consisting of an aqueous

phase and an organic phase, the phosphine hydrochloride (III) passes into the aqueous phase and therefore the aqueous phase is subjected to separation. In the case of other solution forms, separation may be performed as required by adding water, toluene, n-hexane, n-heptane or the like. The aqueous phase resulting from the separation may be washed with toluene, n-hexane, n-heptane or the like as required.

[0079]

The aqueous phase obtained by the reaction of the 1st step contains a reaction intermediate dissolved therein that is assumed to be a phosphine hydrochloride (III) represented by Formula (III):

$$(R^1)(R^2)(R^3)PH \cdot Cl \qquad (III)$$

wherein R^1, R^2 and R^3 are as defined in Formula (II).

[0080]

The formation of the phosphine hydrochloride (III) may be confirmed by, for example, a nuclear magnetic resonance spectrum (^1H-NMR).

[2nd step]

The reaction intermediate that is assumed to be the phosphine hydrochloride (III) obtained in the 1st step is reacted with a tetraarylborate compound (IV) under predetermined conditions to produce a novel phosphonium borate compound (I) of the present invention.

[0081]

The tetraarylborate compound (IV) used in the 2nd step is represented by Formula (IV):

$M \cdot BAr_4$ (IV)

wherein M is lithium, sodium, potassium, magnesium halide or calcium halide, and Ar is an aryl group of 6 to 20 carbon atoms.

[0082]

In Formula (IV), M may be a magnesium halide or a calcium halide, with examples including magnesium fluoride, magnesium chloride, magnesium bromide, magnesium iodide, calcium fluoride, calcium chloride, calcium bromide and calcium iodide.

[0083]

Ar is desirably an aryl group having 6 to 20, preferably 6 to 10 carbon atoms.

[0084]

Specific examples include phenyl, ortho-tolyl, meta-tolyl, para-tolyl, 2,3-xylyl, 2,4-xylyl, 2,5-xylyl, 2,6-xylyl, 3,4-xylyl, 3,5-xylyl, mesityl, 2-tert-butylphenyl, 3-tert-butylphenyl, 4-tert-butylphenyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-tert-butoxyphenyl, 3-tert-butoxyphenyl and 4-tert-butoxyphenyl.

[0085]

The tetraarylborate compound (IV) is selected appropriately such that in Formula (I), R^1, R^2 and R^3 are not tert-butyl groups simultaneously and Ar is not phenyl group at the same time, and R^1, R^2 and R^3 are not cyclohexyl groups simultaneously and Ar is not phenyl group at the same time.

[0086]

Specific examples of the tetraarylborate compounds represented by Formula (IV) are shown in Tables 5 to 10 which will be presented later. These tetraarylborate compounds (IV) may be used singly or in combination of two or more kinds.

[0087]

Of the tetraarylborate compounds (IV), sodium tetraphenylborate and sodium tetra-para-tolylborate are particularly preferable. The tetraarylborate compounds (IV) are preferable because of easy synthesis by known methods.

[0088]

The tetraarylborate compounds (IV) may be used in an undiluted form, or may be diluted with a solvent.

[0089]

The solvent may be appropriately selected from the solvents used for dissolving the phosphines (II). The solvents may be used singly or in combination of two or more kinds.

[0090]

Specifically, the 2nd step involving the above raw materials is performed by mixing the aqueous solution of the reaction intermediate assumed to be the phosphine hydrochloride (III), with the tetraarylborate compound (IV) thereby to react the compound (III) with the compound (IV) under predetermined conditions.

[0091]

The addition sequence of the aqueous solution obtained in the 1st step and the tetraarylborate compound (IV) is not particularly limited. The addition method is not particularly limited, and the material may be added all at once or may be added dropwise intermittently or continuously.

[0092]

In the 2nd step, the desirable requirement of the tetraarylborate compound (IV), desirable temperature for smooth reaction, and desirable time to complete the reaction vary depending on the type of the raw material compound phosphine (II) used, amount of hydrogen chloride gas or hydrochloric acid, and type of the tetraarylborate compound (IV), and are selected appropriately.

[0093]

The amount of the tetraarylborate compound (IV) varies depending on the type of the phosphine (II) used in the 1st step, and is desirably in the range of 0.55 to 5.5 mol,

preferably 0.85 to 1.65 mol per mol of phosphine. Particularly preferably, the compound is used in an amount of at least 1 mol per mol of HCl used. The amount of the tetraarylborate compound (IV) in this range enables the production of the phosphonium borate compound (I) in a high yield.

[0094]

The reaction of the tetraarylborate compound (IV) is desirably carried out while the reaction solution is at -20 to 150°C, preferably 0 to 80°C and is continuously stirred for up to 24 hours, preferably 1 to 5 hours at the temperature. The reaction under these conditions enables the production of the phosphonium borate compound (I) in a high yield.

[0095]

After the completion of the reaction, purification such as recrystallization or column chromatography is performed, and consequently the objective phosphonium borate compound (I) of Formula (I) can be obtained with high purity:

[0096]

$$(R^1)(R^2)(R^3)PH\cdot BAr_4 \qquad (I)$$

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms,

a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^1, R^2 and R^3 may be the same or different from one another;

Ar is an aryl group of 6 to 20 carbon atoms;

[0097]

R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously and Ar cannot be phenyl group at the same time; and

R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously and Ar cannot be phenyl group at the same time.

According to the first production process, the phosphonium borate compound (I) can be obtained in a high yield, specifically in a yield of about 76 to 89 mol% in terms of phosphine (II).

[0098]

The second process for producing the phosphonium borate compounds will be described in detail below. Details common

to the first process will not explained here.

[0099]

<Second production process>

[1'st step]

In the 1'st step, a phosphine (II) and H_2SO_4 are reacted under predetermined conditions.

[0100]

These components will be described below.

[0101]

The phosphine (II) used as a raw material in the production process may be the phosphine compound used in the first production process.

[0102]

H_2SO_4 used in the production process may be sulfuric acid. The concentration thereof is not particularly limited, and is desirably in the range of 0.1 to 95% by weight, preferably 10 to 40% by weight.

[0103]

The 1'st step involving the above raw materials is performed in a reactor purged with an inert gas such as nitrogen or argon. The addition sequence of the raw materials is not particularly limited. For example, sulfuric acid may be added to the phosphine (II), or the phosphine (II) may be added to sulfuric acid. The addition method is not particularly

limited, and the material may be added all at once or may be added dropwise intermittently or continuously.

[0104]

In the 1'st step, the desirable H_2SO_4 requirement, desirable temperature for smooth reaction, and desirable time to complete the reaction vary depending on the type of the phosphine (II) used, and are selected appropriately.

[0105]

The amount of sulfuric acid varies depending on the type of the phosphine (II), and the amount of H_2SO_4 is desirably in the range of 0.25 to 2.5 mol, preferably 0.4 to 0.8 mol per mol of phosphine. The H_2SO_4 amount in this range enables the production of the phosphonium borate compound (I) in a high yield.

[0106]

The reaction of H_2SO_4 is desirably carried out while the solution is at -20 to 150°C, preferably 0 to 80°C and is continuously stirred for up to 24 hours, preferably 30 minutes to 5 hours at the temperature. The reaction under these conditions enables the production of the phosphonium borate compound (I) in a high yield.

[0107]

The completion of the reaction in the 1'st step may be determined by confirming the absence of unreacted phosphine

(II). Specifically, the organic phase is analyzed by gas chromatography or the like to determine the phosphine (II) in the organic phase. When the analysis confirms substantial absence of the remaining phosphine (II), the reaction is terminated. When the phosphine is still present in the organic phase, the reaction is preferably continued.

[0108]

The reaction solution takes various forms depending on the solvent used. For example, the solution may contain crystals of phosphine sulfate (V) (described later), may be a uniform solution or a suspension, or may be a two-phase system consisting of an aqueous phase and an organic phase. In the case of the two-phase system consisting of an aqueous phase and an organic phase, the phosphine sulfate (V) passes into the aqueous phase and therefore the aqueous phase is subjected to separation. In the case of other solution forms, separation may be performed as required by adding water, toluene, n-hexane, n-heptane or the like. The aqueous phase resulting from the separation may be washed with toluene, n-hexane, n-heptane or the like as required.

[0109]

The aqueous phase obtained by the reaction of the 1'st step contains a reaction intermediate dissolved therein that is assumed to be a phosphine sulfate (V) represented by Formula

(V):

$$[(R^1)(R^2)(R^3)PH]_{(2-n)} \cdot H_nSO_4 \qquad (V)$$

wherein R^1, R^2 and R^3 are as defined in Formula (II), and n is an integer of 0 or 1.

[0110]

The formation of the phosphine sulfate (V) may be confirmed by, for example, a nuclear magnetic resonance spectrum (^{1}H-NMR).

[2'nd step]

The reaction intermediate obtained in the 1'st step that is assumed to be the phosphine sulfate (V) is reacted with a tetraarylborate compound (IV) under predetermined conditions to produce a phosphonium borate compound (I) according to the invention.

[0111]

The tetraarylborate compound (IV) used in the 2'nd step may be the same as that used in the 1'st production process.

[0112]

Specifically, the 2'nd step involving the above raw materials is performed by mixing the aqueous solution of the reaction intermediate assumed to be the phosphine sulfate (V), with the tetraarylborate compound (IV) thereby to react the compound (V) with the compound (IV) under predetermined conditions.

[0113]

The addition sequence of the aqueous solution obtained in the 1'st step and the tetraarylborate compound (IV) is not particularly limited. The addition method is not particularly limited, and the material may be added all at once or may be added dropwise intermittently or continuously.

[0114]

In the 2'nd step, the desirable requirement of the tetraarylborate compound (IV), desirable temperature for smooth reaction, and desirable time to complete the reaction vary depending on the type of the raw material compound phosphine (II) used, amount of sulfuric acid, and type of the tetraarylborate compound (IV), and are selected appropriately.

[0115]

The amount of the tetraarylborate compound (IV) varies depending on the type of the phosphine (II) used in the 1'st step, and is desirably in the range of 0.55 to 5.5 mol, preferably 0.85 to 1.65 mol per mol of phosphine. Particularly preferably, the compound is used in an amount of at least 2 mol per mol of H_2SO_4 used. The amount of the tetraarylborate compound (IV) in this range enables the production of the phosphonium borate compound (I) in a high yield.

[0116]

The reaction of the tetraarylborate compound (IV) is desirably carried out while the reaction solution is at −20 to 150°C, preferably 0 to 80°C and is continuously stirred for up to 24 hours, preferably 1 to 5 hours at the temperature. The reaction under these conditions enables the production of the phosphonium borate compound (I) in a high yield.

[0117]

After the completion of the reaction, purification such as recrystallization or column chromatography is performed, and consequently the objective phosphonium borate compound (I) of Formula (I) can be obtained with high purity.

[0118]

According to the second production process, the phosphonium borate compound (I) can be obtained in a high yield, specifically in a yield of about 80 to 85 mol% in terms of phosphine (II).

[0119]

Specific examples of the phosphonium borate compounds (I) of Formula (I) that are obtained by the first and the second production process include those shown in Tables 11 to 18 which will be presented later.

[0120]

The phosphonium borate compounds (I) obtained by the production processes of the invention can be used in

combination with a transition metal, transition metal salt, transition metal oxide or transition metal complex in the carbon-carbon bond forming reactions such as Suzuki-Miyaura reaction, Kumada reaction, Negishi reaction, Hiyama reaction, Kosugi-Stille reaction, Heck reaction, Endo reaction and α-allylation of carbonyl compounds; carbon-nitrogen bond forming reactions such as Buchwald-Hartwig amination; and carbon-oxygen bond forming reactions such as ether synthesis wherein a transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compounds in combination with the transition metal, transition metal salt, transition metal oxide or transition metal complex are used in place of the transition metal complex having a phosphine ligand.

[0121]

The transition metals include fluorides, chlorides, bromides, iodides, sulfates, nitrates, nitrites, carbonates, borates, ammonium salts, sodium salts, potassium salts, acetates, trifluoroacetates, acetylacetone salts, hydride salts, sulfides and cyanides of manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium and platinum. Hydrates of these transition metal salts are also employable. Specific examples include, but are not limited to, manganese (II) chloride, iron (II) chloride, iron (III) chloride, cobalt (II)

chloride, nickel (II) chloride, ruthenium (III) chloride, rhodium (III) chloride, palladium (II) chloride, palladium (II) bromide, manganese (II) acetate, manganese (III) acetate, iron (II) acetate, cobalt (II) acetate, nickel (II) acetate, rhodium (II) acetate dimer, palladium (II) acetate, manganese (II) acetylacetonate, manganese (III) acetylacetonate, iron (II) acetylacetonate, iron (III) acetylacetonate, cobalt (II) acetylacetonate, cobalt (III) acetylacetonate, nickel (II) acetylacetonate, ruthenium (III) acetylacetonate, rhodium (III) acetylacetonate, palladium (II) acetylacetonate, platinum (II) acetylacetonate and sodium (IV) chloroplatinate hexahydrate.

[0122]

The transition metal oxides include oxides of manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium and platinum. Hydrates of these transition metal oxides are also employable. Specific examples include, but are not limited to, manganese (II) oxide, iron (III) oxide, cobalt (II) oxide, nickel (II) oxide, ruthenium (IV) oxide, rhodium (III) oxide, palladium (II) oxide and platinum (IV) oxide.

[0123]

The transition metal complexes include benzonitrile complexes, acetonitrile complexes, triphenylphosphine complexes, ethylene complexes, allyl complexes, butadiene

complexes, cyclopentadiene complexes, cyclooctadiene complexes, cyclooctatetraene complexes, carbonyl complexes, dibenzylideneacetone complexes, amine complexes, ethylenediamine complexes, pyridine complexes and disiloxane complexes of manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium and platinum. Hydrates of these transition metal complexes are also employable. Specific examples include, but are not limited to, decacarbonylmanganese (0), bis(cyclooctatetraene)iron (0), bis(cyclopentadienyl)cobalt (0), bis(cyclooctadiene)nickel (0), bis(cyclopentadienyl)ruthenium (0), tetrarhodiumdodecacarbonyl (0), tris(dibenzylideneacetone)dipalladium (0), bis(benzonitrile)dichloropalladium (II), allylpalladium chloride dimer and divinyltetramethyldisiloxane platinum (0).

[0124]

Tables 1 to 4 below show specific examples of the phosphines of Formula (II) that are used as starting compounds in the present invention. Tables 5 to 10 below show specific examples of the tetraarylborate compounds of Formula (IV). Tables 11 to 18 below show specific examples of the phosphonium borate compounds (I) according to the present invention.

[0125]

Specific examples of the phosphines (II) represented by

Formula (II):

$$(R^1)(R^2)(R^3)P \qquad \text{(II)}$$

include, but are not limited to, the following compounds.

[0126] [Table 1-1]

Table 1-1

R^1	R^2	R^3
tert-butyl	tert-butyl	hydrogen
tert-butyl	tert-butyl	methyl
tert-butyl	tert-butyl	ethyl
tert-butyl	tert-butyl	n-propyl
tert-butyl	tert-butyl	n-butyl
tert-butyl	tert-butyl	isobutyl
tert-butyl	tert-butyl	n-pentyl
tert-butyl	tert-butyl	isopentyl
tert-butyl	tert-butyl	n-hexyl
tert-butyl	tert-butyl	2-methyl-1-pentyl
tert-butyl	tert-butyl	2,2-diethyl-1-ethyl
tert-butyl	tert-butyl	n-heptyl
tert-butyl	tert-butyl	n-octyl
tert-butyl	tert-butyl	isopropyl
tert-butyl	tert-butyl	sec-butyl
tert-butyl	tert-butyl	2-pentyl
tert-butyl	tert-butyl	3-pentyl
tert-butyl	tert-butyl	2-hexyl
tert-butyl	tert-butyl	3-hexyl
tert-butyl	tert-butyl	tert-butyl
tert-butyl	tert-butyl	tert-amyl
tert-butyl	tert-butyl	1,1-dimethylbutyl
tert-butyl	tert-butyl	3-methyl-3-pentyl
tert-butyl	tert-butyl	1,1,2-trimethylpropyl
tert-butyl	tert-butyl	1-adamantyl
tert-butyl	tert-butyl	2-methyl-1-adamantyl
tert-butyl	tert-butyl	cyclopropyl
tert-butyl	tert-butyl	cyclopentyl
tert-butyl	tert-butyl	cyclohexyl
tert-butyl	tert-butyl	1-methylcyclohexyl
tert-butyl	tert-butyl	2-methylcyclohexyl
tert-butyl	tert-butyl	2-adamantyl
tert-butyl	tert-butyl	1-methyl-2-adamantyl
tert-butyl	tert-butyl	2-methyl-2-adamantyl
tert-butyl	tert-butyl	phenyl
tert-butyl	tert-butyl	ortho-tolyl
tert-butyl	tert-butyl	meta-tolyl
tert-butyl	tert-butyl	para-tolyl
tert-butyl	tert-butyl	2,3-xylyl
tert-butyl	tert-butyl	2,4-xylyl
tert-butyl	tert-butyl	2,5-xylyl
tert-butyl	tert-butyl	2,6-xylyl
tert-butyl	tert-butyl	3,4-xylyl
tert-butyl	tert-butyl	3,5-xylyl
tert-butyl	tert-butyl	mesityl

[0127] [Table 1-2]

Table 1-2

R^1	R^2	R^3
tert-butyl	tert-butyl	2-tert-butylphenyl
tert-butyl	tert-butyl	3-tert-butylphenyl
tert-butyl	tert-butyl	4-tert-butylphenyl
tert-butyl	tert-butyl	2-ethenylphenyl
tert-butyl	tert-butyl	3-ethenylphenyl
tert-butyl	tert-butyl	4-ethenylphenyl
tert-butyl	tert-butyl	2-biphenylyl
tert-butyl	tert-butyl	3-biphenylyl
tert-butyl	tert-butyl	4-biphenylyl
tert-butyl	tert-butyl	1-naphthyl
tert-butyl	tert-butyl	2-naphthyl
tert-butyl	tert-butyl	1,1′-binaphthalene-2-yl
tert-butyl	tert-butyl	2-methoxyphenyl
tert-butyl	tert-butyl	3-methoxyphenyl
tert-butyl	tert-butyl	4-methoxyphenyl
tert-butyl	tert-butyl	2-tert-butoxyphenyl
tert-butyl	tert-butyl	3-tert-butoxyphenyl
tert-butyl	tert-butyl	4-tert-butoxyphenyl
tert-butyl	tert-butyl	2-dimethylaminophenyl
tert-butyl	tert-butyl	3-dimethylaminophenyl
tert-butyl	tert-butyl	4-dimethylaminophenyl
tert-butyl	tert-butyl	2′-dimethylamino-2-biphenylyl
tert-butyl	tert-butyl	8-dimethylamino-1-naphthyl
tert-butyl	tert-butyl	2′-dimethylamino-1,1′-binaphthalene-2-yl
tert-butyl	tert-butyl	benzyl
tert-butyl	tert-butyl	1-phenylethyl
tert-butyl	tert-butyl	2-phenylethyl
tert-butyl	tert-butyl	2-ethenylbenzyl
tert-butyl	tert-butyl	3-ethenylbenzyl
tert-butyl	tert-butyl	4-ethenylbenzyl
tert-butyl	tert-butyl	4-(2-ethenylphenyl)butyl
tert-butyl	tert-butyl	4-(3-ethenylphenyl)butyl
tert-butyl	tert-butyl	4-(4-ethenylphenyl)butyl
tert-butyl	tert-butyl	vinyl
tert-butyl	tert-butyl	methallyl
tert-butyl	tert-butyl	1-octenyl
tert-butyl	tert-butyl	ethynyl
tert-butyl	tert-butyl	1-propynyl
tert-butyl	tert-butyl	1-octynyl
tert-butyl	tert-butyl	allyl
tert-butyl	tert-butyl	2-octenyl
isopropyl	isopropyl	isopropyl
cyclohexyl	cyclohexyl	cyclohexyl

[0128] [Table 2-1]

Table 2-1

R^1	R^2	R^3
tert-amyl	tert-amyl	hydrogen
tert-amyl	tert-amyl	methyl
tert-amyl	tert-amyl	ethyl
tert-amyl	tert-amyl	n-propyl
tert-amyl	tert-amyl	n-butyl
tert-amyl	tert-amyl	isobutyl
tert-amyl	tert-amyl	n-pentyl
tert-amyl	tert-amyl	isopentyl
tert-amyl	tert-amyl	n-hexyl
tert-amyl	tert-amyl	2-methyl-1-pentyl
tert-amyl	tert-amyl	2,2-diethyl-1-ethyl
tert-amyl	tert-amyl	n-heptyl
tert-amyl	tert-amyl	n-octyl
tert-amyl	tert-amyl	isopropyl
tert-amyl	tert-amyl	sec-butyl
tert-amyl	tert-amyl	2-pentyl
tert-amyl	tert-amyl	3-pentyl
tert-amyl	tert-amyl	2-hexyl
tert-amyl	tert-amyl	3-hexyl
tert-amyl	tert-amyl	tert-butyl
tert-amyl	tert-amyl	tert-amyl
tert-amyl	tert-amyl	1,1-dimethylbutyl
tert-amyl	tert-amyl	3-methyl-3-pentyl
tert-amyl	tert-amyl	1,1,2-trimethylpropyl
tert-amyl	tert-amyl	1-adamantyl
tert-amyl	tert-amyl	2-methyl-1-adamantyl
tert-amyl	tert-amyl	cyclopropyl
tert-amyl	tert-amyl	cyclopentyl
tert-amyl	tert-amyl	cyclohexyl
tert-amyl	tert-amyl	1-methylcyclohexyl
tert-amyl	tert-amyl	2-methylcyclohexyl
tert-amyl	tert-amyl	2-adamantyl
tert-amyl	tert-amyl	1-methyl-2-adamantyl
tert-amyl	tert-amyl	2-methyl-2-adamantyl
tert-amyl	tert-amyl	phenyl
tert-amyl	tert-amyl	ortho-tolyl
tert-amyl	tert-amyl	meta-tolyl
tert-amyl	tert-amyl	para-tolyl
tert-amyl	tert-amyl	2,3-xylyl
tert-amyl	tert-amyl	2,4-xylyl
tert-amyl	tert-amyl	2,5-xylyl
tert-amyl	tert-amyl	2,6-xylyl
tert-amyl	tert-amyl	3,4-xylyl

[0129] [Table 2-2]

Table 2-2

R^1	R^2	R^3
tert-amyl	tert-amyl	3,5-xylyl
tert-amyl	tert-amyl	mesityl
tert-amyl	tert-amyl	2-tert-butylphenyl
tert-amyl	tert-amyl	3-tert-butylphenyl
tert-amyl	tert-amyl	4-tert-butylphenyl
tert-amyl	tert-amyl	2-ethenylphenyl
tert-amyl	tert-amyl	3-ethenylphenyl
tert-amyl	tert-amyl	4-ethenylphenyl
tert-amyl	tert-amyl	2-biphenylyl
tert-amyl	tert-amyl	3-biphenylyl
tert-amyl	tert-amyl	4-biphenylyl
tert-amyl	tert-amyl	1-naphthyl
tert-amyl	tert-amyl	2-naphthyl
tert-amyl	tert-amyl	1,1′-binaphthalene-2-yl
tert-amyl	tert-amyl	2-methoxyphenyl
tert-amyl	tert-amyl	3-methoxyphenyl
tert-amyl	tert-amyl	4-methoxyphenyl
tert-amyl	tert-amyl	2-tert-butoxyphenyl
tert-amyl	tert-amyl	3-tert-butoxyphenyl
tert-amyl	tert-amyl	4-tert-butoxyphenyl
tert-amyl	tert-amyl	2-dimethylaminophenyl
tert-amyl	tert-amyl	3-dimethylaminophenyl
tert-amyl	tert-amyl	4-dimethylaminophenyl
tert-amyl	tert-amyl	2′-dimethylamino-2-biphenylyl
tert-amyl	tert-amyl	8-dimethylamino-1-naphthyl
tert-amyl	tert-amyl	2′-dimethylamino-1,1′-binaphthalene-2-yl
tert-amyl	tert-amyl	benzyl
tert-amyl	tert-amyl	1-phenylethyl
tert-amyl	tert-amyl	2-phenylethyl
tert-amyl	tert-amyl	2-ethenylbenzyl
tert-amyl	tert-amyl	3-ethenylbenzyl
tert-amyl	tert-amyl	4-ethenylbenzyl
tert-amyl	tert-amyl	4-(2-ethenylphenyl)butyl
tert-amyl	tert-amyl	4-(3-ethenylphenyl)butyl
tert-amyl	tert-amyl	4-(4-ethenylphenyl)butyl
tert-amyl	tert-amyl	vinyl
tert-amyl	tert-amyl	methallyl
tert-amyl	tert-amyl	1-octenyl
tert-amyl	tert-amyl	ethynyl
tert-amyl	tert-amyl	1-propynyl
tert-amyl	tert-amyl	1-octynyl
tert-amyl	tert-amyl	allyl
tert-amyl	tert-amyl	2-octenyl

[0130] [Table 3-1]

Table 3-1

R^1	R^2	R^3
1-adamantyl	1-adamantyl	hydrogen
1-adamantyl	1-adamantyl	methyl
1-adamantyl	1-adamantyl	ethyl
1-adamantyl	1-adamantyl	n-propyl
1-adamantyl	1-adamantyl	n-butyl
1-adamantyl	1-adamantyl	isobutyl
1-adamantyl	1-adamantyl	n-pentyl
1-adamantyl	1-adamantyl	isopentyl
1-adamantyl	1-adamantyl	n-hexyl
1-adamantyl	1-adamantyl	2-methyl-1-pentyl
1-adamantyl	1-adamantyl	2,2-diethyl-1-ethyl
1-adamantyl	1-adamantyl	n-heptyl
1-adamantyl	1-adamantyl	n-octyl
1-adamantyl	1-adamantyl	isopropyl
1-adamantyl	1-adamantyl	sec-butyl
1-adamantyl	1-adamantyl	2-pentyl
1-adamantyl	1-adamantyl	3-pentyl
1-adamantyl	1-adamantyl	2-hexyl
1-adamantyl	1-adamantyl	3-hexyl
1-adamantyl	1-adamantyl	tert-butyl
1-adamantyl	1-adamantyl	tert-amyl
1-adamantyl	1-adamantyl	1,1-dimethylbutyl
1-adamantyl	1-adamantyl	3-methyl-3-pentyl
1-adamantyl	1-adamantyl	1,1,2-trimethylpropyl
1-adamantyl	1-adamantyl	1-adamantyl
1-adamantyl	1-adamantyl	2-methyl-1-adamantyl
1-adamantyl	1-adamantyl	cyclopropyl
1-adamantyl	1-adamantyl	cyclopentyl
1-adamantyl	1-adamantyl	cyclohexyl
1-adamantyl	1-adamantyl	1-methylcyclohexyl
1-adamantyl	1-adamantyl	2-methylcyclohexyl
1-adamantyl	1-adamantyl	2-adamantyl
1-adamantyl	1-adamantyl	1-methyl-2-adamantyl
1-adamantyl	1-adamantyl	2-methyl-2-adamantyl
1-adamantyl	1-adamantyl	phenyl
1-adamantyl	1-adamantyl	ortho-tolyl
1-adamantyl	1-adamantyl	meta-tolyl
1-adamantyl	1-adamantyl	para-tolyl
1-adamantyl	1-adamantyl	2,3-xylyl
1-adamantyl	1-adamantyl	2,4-xylyl
1-adamantyl	1-adamantyl	2,5-xylyl
1-adamantyl	1-adamantyl	2,6-xylyl
1-adamantyl	1-adamantyl	3,4-xylyl
1-adamantyl	1-adamantyl	3,5-xylyl
1-adamantyl	1-adamantyl	mesityl

[0131] [Table 3-2]

Table 3-2

R^1	R^2	R^3
1-adamantyl	1-adamantyl	2-tert-butylphenyl
1-adamantyl	1-adamantyl	3-tert-butylphenyl
1-adamantyl	1-adamantyl	4-tert-butylphenyl
1-adamantyl	1-adamantyl	2-ethenylphenyl
1-adamantyl	1-adamantyl	3-ethenylphenyl
1-adamantyl	1-adamantyl	4-ethenylphenyl
1-adamantyl	1-adamantyl	2-biphenylyl
1-adamantyl	1-adamantyl	3-biphenylyl
1-adamantyl	1-adamantyl	4-biphenylyl
1-adamantyl	1-adamantyl	1-naphthyl
1-adamantyl	1-adamantyl	2-naphthyl
1-adamantyl	1-adamantyl	1,1'-binaphthalene-2-yl
1-adamantyl	1-adamantyl	2-methoxyphenyl
1-adamantyl	1-adamantyl	3-methoxyphenyl
1-adamantyl	1-adamantyl	4-methoxyphenyl
1-adamantyl	1-adamantyl	2-tert-butoxyphenyl
1-adamantyl	1-adamantyl	3-tert-butoxyphenyl
1-adamantyl	1-adamantyl	4-tert-butoxyphenyl
1-adamantyl	1-adamantyl	2-dimethylaminophenyl
1-adamantyl	1-adamantyl	3-dimethylaminophenyl
1-adamantyl	1-adamantyl	4-dimethylaminophenyl
1-adamantyl	1-adamantyl	2'-dimethylamino-2-biphenylyl
1-adamantyl	1-adamantyl	8-dimethylamino-1-naphthyl
1-adamantyl	1-adamantyl	2'-dimethylamino-1,1'-binaphthalene-2-yl
1-adamantyl	1-adamantyl	benzyl
1-adamantyl	1-adamantyl	1-phenylethyl
1-adamantyl	1-adamantyl	2-phenylethyl
1-adamantyl	1-adamantyl	2-ethenylbenzyl
1-adamantyl	1-adamantyl	3-ethenylbenzyl
1-adamantyl	1-adamantyl	4-ethenylbenzyl
1-adamantyl	1-adamantyl	4-(2-ethenylphenyl)butyl
1-adamantyl	1-adamantyl	4-(3-ethenylphenyl)butyl
1-adamantyl	1-adamantyl	4-(4-ethenylphenyl)butyl
1-adamantyl	1-adamantyl	vinyl
1-adamantyl	1-adamantyl	methallyl
1-adamantyl	1-adamantyl	1-octenyl
1-adamantyl	1-adamantyl	ethynyl
1-adamantyl	1-adamantyl	1-propynyl
1-adamantyl	1-adamantyl	1-octynyl
1-adamantyl	1-adamantyl	allyl
1-adamantyl	1-adamantyl	2-octenyl

[0132] [Table 4-1]

Table 4-1

R^1	R^2	R^3
2-adamantyl	2-adamantyl	hydrogen
2-adamantyl	2-adamantyl	methyl
2-adamantyl	2-adamantyl	ethyl
2-adamantyl	2-adamantyl	n-propyl
2-adamantyl	2-adamantyl	n-butyl
2-adamantyl	2-adamantyl	isobutyl
2-adamantyl	2-adamantyl	n-pentyl
2-adamantyl	2-adamantyl	isopentyl
2-adamantyl	2-adamantyl	n-hexyl
2-adamantyl	2-adamantyl	2-methyl-1-pentyl
2-adamantyl	2-adamantyl	2,2-diethyl-1-ethyl
2-adamantyl	2-adamantyl	n-heptyl
2-adamantyl	2-adamantyl	n-octyl
2-adamantyl	2-adamantyl	isopropyl
2-adamantyl	2-adamantyl	sec-butyl
2-adamantyl	2-adamantyl	2-pentyl
2-adamantyl	2-adamantyl	3-pentyl
2-adamantyl	2-adamantyl	2-hexyl
2-adamantyl	2-adamantyl	3-hexyl
2-adamantyl	2-adamantyl	tert-butyl
2-adamantyl	2-adamantyl	tert-amyl
2-adamantyl	2-adamantyl	1,1-dimethylbutyl
2-adamantyl	2-adamantyl	3-methyl-3-pentyl
2-adamantyl	2-adamantyl	1,1,2-trimethylpropyl
2-adamantyl	2-adamantyl	1-adamantyl
2-adamantyl	2-adamantyl	2-methyl-1-adamantyl
2-adamantyl	2-adamantyl	cyclopropyl
2-adamantyl	2-adamantyl	cyclopentyl
2-adamantyl	2-adamantyl	cyclohexyl
2-adamantyl	2-adamantyl	1-methylcyclohexyl
2-adamantyl	2-adamantyl	2-methylcyclohexyl
2-adamantyl	2-adamantyl	2-adamantyl
2-adamantyl	2-adamantyl	1-methyl-2-adamantyl
2-adamantyl	2-adamantyl	2-methyl-2-adamantyl
2-adamantyl	2-adamantyl	phenyl
2-adamantyl	2-adamantyl	ortho-tolyl
2-adamantyl	2-adamantyl	meta-tolyl
2-adamantyl	2-adamantyl	para-tolyl
2-adamantyl	2-adamantyl	2,3-xylyl
2-adamantyl	2-adamantyl	2,4-xylyl
2-adamantyl	2-adamantyl	2,5-xylyl
2-adamantyl	2-adamantyl	2,6-xylyl
2-adamantyl	2-adamantyl	3,4-xylyl
2-adamantyl	2-adamantyl	3,5-xylyl
2-adamantyl	2-adamantyl	mesityl

[0133] [Table 4-2]

Table 4-2

R^1	R^2	R^3
2-adamantyl	2-adamantyl	2-tert-butylphenyl
2-adamantyl	2-adamantyl	3-tert-butylphenyl
2-adamantyl	2-adamantyl	4-tert-butylphenyl
2-adamantyl	2-adamantyl	2-ethenylphenyl
2-adamantyl	2-adamantyl	3-ethenylphenyl
2-adamantyl	2-adamantyl	4-ethenylphenyl
2-adamantyl	2-adamantyl	2-biphenylyl
2-adamantyl	2-adamantyl	3-biphenylyl
2-adamantyl	2-adamantyl	4-biphenylyl
2-adamantyl	2-adamantyl	1-naphthyl
2-adamantyl	2-adamantyl	2-naphthyl
2-adamantyl	2-adamantyl	1,1'-binaphthalene-2-yl
2-adamantyl	2-adamantyl	2-methoxyphenyl
2-adamantyl	2-adamantyl	3-methoxyphenyl
2-adamantyl	2-adamantyl	4-methoxyphenyl
2-adamantyl	2-adamantyl	2-tert-butoxyphenyl
2-adamantyl	2-adamantyl	3-tert-butoxyphenyl
2-adamantyl	2-adamantyl	4-tert-butoxyphenyl
2-adamantyl	2-adamantyl	2-dimethylaminophenyl
2-adamantyl	2-adamantyl	3-dimethylaminophenyl
2-adamantyl	2-adamantyl	4-dimethylaminophenyl
2-adamantyl	2-adamantyl	2'-dimethylamino-2-biphenylyl
2-adamantyl	2-adamantyl	8-dimethylamino-1-naphthyl
2-adamantyl	2-adamantyl	2'-dimethylamino-1,1'-binaphthalene-2-yl
2-adamantyl	2-adamantyl	benzyl
2-adamantyl	2-adamantyl	1-phenylethyl
2-adamantyl	2-adamantyl	2-phenylethyl
2-adamantyl	2-adamantyl	2-ethenylbenzyl
2-adamantyl	2-adamantyl	3-ethenylbenzyl
2-adamantyl	2-adamantyl	4-ethenylbenzyl
2-adamantyl	2-adamantyl	4-(2-ethenylphenyl)butyl
2-adamantyl	2-adamantyl	4-(3-ethenylphenyl)butyl
2-adamantyl	2-adamantyl	4-(4-ethenylphenyl)butyl
2-adamantyl	2-adamantyl	vinyl
2-adamantyl	2-adamantyl	methallyl
2-adamantyl	2-adamantyl	1-octenyl
2-adamantyl	2-adamantyl	ethynyl
2-adamantyl	2-adamantyl	1-propynyl
2-adamantyl	2-adamantyl	1-octynyl
2-adamantyl	2-adamantyl	allyl
2-adamantyl	2-adamantyl	2-octenyl

[0134]

Tables 5 to 10 below show specific examples of the tetraarylborate compounds of Formula (IV):

$M \cdot BAr_4$ (IV)

that are used as starting compounds in the present invention. The compounds are not limited thereto.

[0135] [Table 5]

Table 5

Ar	M
phenyl	lithium
ortho-tolyl	lithium
meta-tolyl	lithium
para-tolyl	lithium
2,3-xylyl	lithium
2,4-xylyl	lithium
2,5-xylyl	lithium
2,6-xylyl	lithium
3,4-xylyl	lithium
3,5-xylyl	lithium
mesityl	lithium
2-tert-butylphenyl	lithium
3-tert-butylphenyl	lithium
4-tert-butylphenyl	lithium
2-methoxyphenyl	lithium
3-methoxyphenyl	lithium
4-methoxyphenyl	lithium
2-tert-butoxyphenyl	lithium
3-tert-butoxyphenyl	lithium
4-tert-butoxyphenyl	lithium

[0136] [Table 6]

Table 6

Ar	M
phenyl	sodium
ortho-tolyl	sodium
meta-tolyl	sodium
para-tolyl	sodium
2,3-xylyl	sodium
2,4-xylyl	sodium
2,5-xylyl	sodium
2,6-xylyl	sodium
3,4-xylyl	sodium
3,5-xylyl	sodium
mesityl	sodium
2-tert-butylphenyl	sodium
3-tert-butylphenyl	sodium
4-tert-butylphenyl	sodium
2-methoxyphenyl	sodium
3-methoxyphenyl	sodium
4-methoxyphenyl	sodium
2-tert-butoxyphenyl	sodium
3-tert-butoxyphenyl	sodium
4-tert-butoxyphenyl	sodium

[0137] [Table 7]

Table 7

Ar	M
phenyl	potassium
ortho-tolyl	potassium
meta-tolyl	potassium
para-tolyl	potassium
2,3-xylyl	potassium
2,4-xylyl	potassium
2,5-xylyl	potassium
2,6-xylyl	potassium
3,4-xylyl	potassium
3,5-xylyl	potassium
mesityl	potassium
2-tert-butylphenyl	potassium
3-tert-butylphenyl	potassium
4-tert-butylphenyl	potassium
2-methoxyphenyl	potassium
3-methoxyphenyl	potassium
4-methoxyphenyl	potassium
2-tert-butoxyphenyl	potassium
3-tert-butoxyphenyl	potassium
4-tert-butoxyphenyl	potassium

[0138] [Table 8]

Table 8

Ar	M
phenyl	magnesium chloride
ortho-tolyl	magnesium chloride
meta-tolyl	magnesium chloride
para-tolyl	magnesium chloride
2,3-xylyl	magnesium chloride
2,4-xylyl	magnesium chloride
2,5-xylyl	magnesium chloride
2,6-xylyl	magnesium chloride
3,4-xylyl	magnesium chloride
3,5-xylyl	magnesium chloride
mesityl	magnesium chloride
2-tert-butylphenyl	magnesium chloride
3-tert-butylphenyl	magnesium chloride
4-tert-butylphenyl	magnesium chloride
2-methoxyphenyl	magnesium chloride
3-methoxyphenyl	magnesium chloride
4-methoxyphenyl	magnesium chloride
2-tert-butoxyphenyl	magnesium chloride
3-tert-butoxyphenyl	magnesium chloride
4-tert-butoxyphenyl	magnesium chloride

[0139] [Table 9]

Table 9

Ar	M
phenyl	magnesium bromide
ortho-tolyl	magnesium bromide
meta-tolyl	magnesium bromide
para-tolyl	magnesium bromide
2,3-xylyl	magnesium bromide
2,4-xylyl	magnesium bromide
2,5-xylyl	magnesium bromide
2,6-xylyl	magnesium bromide
3,4-xylyl	magnesium bromide
3,5-xylyl	magnesium bromide
mesityl	magnesium bromide
2-tert-butylphenyl	magnesium bromide
3-tert-butylphenyl	magnesium bromide
4-tert-butylphenyl	magnesium bromide
2-methoxyphenyl	magnesium bromide
3-methoxyphenyl	magnesium bromide
4-methoxyphenyl	magnesium bromide
2-tert-butoxyphenyl	magnesium bromide
3-tert-butoxyphenyl	magnesium bromide
4-tert-butoxyphenyl	magnesium bromide

[0140] [Table 10]

Table 10

Ar	M
phenyl	calcium chloride
ortho-tolyl	calcium chloride
meta-tolyl	calcium chloride
para-tolyl	calcium chloride
2,3-xylyl	calcium chloride
2,4-xylyl	calcium chloride
2,5-xylyl	calcium chloride
2,6-xylyl	calcium chloride
3,4-xylyl	calcium chloride
3,5-xylyl	calcium chloride
mesityl	calcium chloride
2-tert-butylphenyl	calcium chloride
3-tert-butylphenyl	calcium chloride
4-tert-butylphenyl	calcium chloride
2-methoxyphenyl	calcium chloride
3-methoxyphenyl	calcium chloride
4-methoxyphenyl	calcium chloride
2-tert-butoxyphenyl	calcium chloride
3-tert-butoxyphenyl	calcium chloride
4-tert-butoxyphenyl	calcium chloride

[0141]

Tables 11 to 18 below show specific examples of the novel phosphonium borate compounds represented by Formula (I):

$$(R^1)(R^2)(R^3)PH\cdot BAr_4 \qquad (I)$$

that are produced according to the present invention. The compounds are not limited thereto.

[0142] [Table 11-1]

Table 11-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-butyl	tert-butyl	hydrogen	phenyl	
tert-butyl	tert-butyl	methyl	phenyl	192-196
tert-butyl	tert-butyl	ethyl	phenyl	174-188
tert-butyl	tert-butyl	n-propyl	phenyl	
tert-butyl	tert-butyl	n-butyl	phenyl	156-162
tert-butyl	tert-butyl	isobutyl	phenyl	
tert-butyl	tert-butyl	n-pentyl	phenyl	
tert-butyl	tert-butyl	isopentyl	phenyl	
tert-butyl	tert-butyl	n-hexyl	phenyl	
tert-butyl	tert-butyl	2-methyl-1-pentyl	phenyl	
tert-butyl	tert-butyl	2,2-diethyl-1-ethyl	phenyl	
tert-butyl	tert-butyl	n-heptyl	phenyl	
tert-butyl	tert-butyl	n-octyl	phenyl	108-113
tert-butyl	tert-butyl	isopropyl	phenyl	
tert-butyl	tert-butyl	sec-butyl	phenyl	184-187
tert-butyl	tert-butyl	2-pentyl	phenyl	
tert-butyl	tert-butyl	3-pentyl	phenyl	
tert-butyl	tert-butyl	2-hexyl	phenyl	
tert-butyl	tert-butyl	3-hexyl	phenyl	
tert-butyl	tert-butyl	tert-amyl	phenyl	
tert-butyl	tert-butyl	1,1-dimethylbutyl	phenyl	
tert-butyl	tert-butyl	3-methyl-3-pentyl	phenyl	
tert-butyl	tert-butyl	1,1,2-trimethylpropyl	phenyl	
tert-butyl	tert-butyl	1-adamantyl	phenyl	
tert-butyl	tert-butyl	2-methyl-1-adamantyl	phenyl	
tert-butyl	tert-butyl	cyclopropyl	phenyl	
tert-butyl	tert-butyl	cyclopentyl	phenyl	
tert-butyl	tert-butyl	cyclohexyl	phenyl	171-178
tert-butyl	tert-butyl	1-methylcyclohexyl	phenyl	
tert-butyl	tert-butyl	2-methylcyclohexyl	phenyl	
tert-butyl	tert-butyl	2-adamantyl	phenyl	
tert-butyl	tert-butyl	1-methyl-2-adamantyl	phenyl	

[0143] [Table 11-2]

Table 11-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-butyl	tert-butyl	2-methyl-2-adamantyl	phenyl	
tert-butyl	tert-butyl	phenyl	phenyl	135-140
tert-butyl	tert-butyl	ortho-tolyl	phenyl	
tert-butyl	tert-butyl	meta-tolyl	phenyl	
tert-butyl	tert-butyl	para-tolyl	phenyl	
tert-butyl	tert-butyl	2,3-xylyl	phenyl	
tert-butyl	tert-butyl	2,4-xylyl	phenyl	
tert-butyl	tert-butyl	2,5-xylyl	phenyl	
tert-butyl	tert-butyl	2,6-xylyl	phenyl	
tert-butyl	tert-butyl	3,4-xylyl	phenyl	
tert-butyl	tert-butyl	3,5-xylyl	phenyl	
tert-butyl	tert-butyl	mesityl	phenyl	
tert-butyl	tert-butyl	2-tert-butylphenyl	phenyl	
tert-butyl	tert-butyl	3-tert-butylphenyl	phenyl	
tert-butyl	tert-butyl	4-tert-butylphenyl	phenyl	
tert-butyl	tert-butyl	2-ethenylphenyl	phenyl	
tert-butyl	tert-butyl	3-ethenylphenyl	phenyl	
tert-butyl	tert-butyl	4-ethenylphenyl	phenyl	
tert-butyl	tert-butyl	2-biphenylyl	phenyl	163-174
tert-butyl	tert-butyl	3-biphenylyl	phenyl	
tert-butyl	tert-butyl	4-biphenylyl	phenyl	
tert-butyl	tert-butyl	1-naphthyl	phenyl	165-174
tert-butyl	tert-butyl	2-naphthyl	phenyl	
tert-butyl	tert-butyl	1,1′-binaphthalene-2-yl	phenyl	
tert-butyl	tert-butyl	2-methoxyphenyl	phenyl	
tert-butyl	tert-butyl	3-methoxyphenyl	phenyl	
tert-butyl	tert-butyl	4-methoxyphenyl	phenyl	
tert-butyl	tert-butyl	2-tert-butoxyphenyl	phenyl	
tert-butyl	tert-butyl	3-tert-butoxyphenyl	phenyl	
tert-butyl	tert-butyl	4-tert-butoxyphenyl	phenyl	

[0144] [Table 11-3]

Table 11-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-butyl	tert-butyl	2-dimethylaminophenyl	phenyl	
tert-butyl	tert-butyl	3-dimethylaminophenyl	phenyl	
tert-butyl	tert-butyl	4-dimethylaminophenyl	phenyl	
tert-butyl	tert-butyl	2′-dimethylamino-2-biphenylyl	phenyl	
tert-butyl	tert-butyl	8-dimethylamino-1-naphthyl	phenyl	
tert-butyl	tert-butyl	2′-dimethylamino-1,1′-binaphthalene-2-yl	phenyl	
tert-butyl	tert-butyl	benzyl	phenyl	149-158
tert-butyl	tert-butyl	1-phenylethyl	phenyl	
tert-butyl	tert-butyl	2-phenylethyl	phenyl	
tert-butyl	tert-butyl	2-ethenylbenzyl	phenyl	
tert-butyl	tert-butyl	3-ethenylbenzyl	phenyl	
tert-butyl	tert-butyl	4-ethenylbenzyl	phenyl	122-132
tert-butyl	tert-butyl	4-(2-ethenylphenyl)butyl	phenyl	
tert-butyl	tert-butyl	4-(3-ethenylphenyl)butyl	phenyl	
tert-butyl	tert-butyl	4-(4-ethenylphenyl)butyl	phenyl	
tert-butyl	tert-butyl	vinyl	phenyl	253-261
tert-butyl	tert-butyl	methallyl	phenyl	
tert-butyl	tert-butyl	1-octenyl	phenyl	
tert-butyl	tert-butyl	ethynyl	phenyl	
tert-butyl	tert-butyl	1-propynyl	phenyl	
tert-butyl	tert-butyl	1-octynyl	phenyl	
tert-butyl	tert-butyl	allyl	phenyl	148-160
tert-butyl	tert-butyl	2-octenyl	phenyl	
isopropyl	isopropyl	isopropyl	phenyl	194-214

[0145] [Table 12-1]

Table 12-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-amyl	tert-amyl	hydrogen	phenyl	
tert-amyl	tert-amyl	methyl	phenyl	
tert-amyl	tert-amyl	ethyl	phenyl	
tert-amyl	tert-amyl	n-propyl	phenyl	
tert-amyl	tert-amyl	n-butyl	phenyl	
tert-amyl	tert-amyl	isobutyl	phenyl	
tert-amyl	tert-amyl	n-pentyl	phenyl	
tert-amyl	tert-amyl	isopentyl	phenyl	
tert-amyl	tert-amyl	n-hexyl	phenyl	
tert-amyl	tert-amyl	2-methyl-1-pentyl	phenyl	
tert-amyl	tert-amyl	2,2-diethyl-1-ethyl	phenyl	
tert-amyl	tert-amyl	n-heptyl	phenyl	
tert-amyl	tert-amyl	n-octyl	phenyl	
tert-amyl	tert-amyl	isopropyl	phenyl	
tert-amyl	tert-amyl	sec-butyl	phenyl	
tert-amyl	tert-amyl	2-pentyl	phenyl	
tert-amyl	tert-amyl	3-pentyl	phenyl	
tert-amyl	tert-amyl	2-hexyl	phenyl	
tert-amyl	tert-amyl	3-hexyl	phenyl	
tert-amyl	tert-amyl	tert-butyl	phenyl	
tert-amyl	tert-amyl	tert-amyl	phenyl	
tert-amyl	tert-amyl	1,1-dimethylbutyl	phenyl	
tert-amyl	tert-amyl	3-methyl-3-pentyl	phenyl	
tert-amyl	tert-amyl	1,1,2-trimethylpropyl	phenyl	
tert-amyl	tert-amyl	1-adamantyl	phenyl	
tert-amyl	tert-amyl	2-methyl-1-adamantyl	phenyl	
tert-amyl	tert-amyl	cyclopropyl	phenyl	
tert-amyl	tert-amyl	cyclopentyl	phenyl	
tert-amyl	tert-amyl	cyclohexyl	phenyl	
tert-amyl	tert-amyl	1-methylcyclohexyl	phenyl	
tert-amyl	tert-amyl	2-methylcyclohexyl	phenyl	
tert-amyl	tert-amyl	2-adamantyl	phenyl	
tert-amyl	tert-amyl	1-methyl-2-adamantyl	phenyl	
tert-amyl	tert-amyl	2-methyl-2-adamantyl	phenyl	

[0146] [Table 12-2]

Table 12-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-amyl	tert-amyl	phenyl	phenyl	
tert-amyl	tert-amyl	ortho-tolyl	phenyl	
tert-amyl	tert-amyl	meta-tolyl	phenyl	
tert-amyl	tert-amyl	para-tolyl	phenyl	
tert-amyl	tert-amyl	2,3-xylyl	phenyl	
tert-amyl	tert-amyl	2,4-xylyl	phenyl	
tert-amyl	tert-amyl	2,5-xylyl	phenyl	
tert-amyl	tert-amyl	2,6-xylyl	phenyl	
tert-amyl	tert-amyl	3,4-xylyl	phenyl	
tert-amyl	tert-amyl	3,5-xylyl	phenyl	
tert-amyl	tert-amyl	mesityl	phenyl	
tert-amyl	tert-amyl	2-tert-butylphenyl	phenyl	
tert-amyl	tert-amyl	3-tert-butylphenyl	phenyl	
tert-amyl	tert-amyl	4-tert-butylphenyl	phenyl	
tert-amyl	tert-amyl	2-ethenylphenyl	phenyl	
tert-amyl	tert-amyl	3-ethenylphenyl	phenyl	
tert-amyl	tert-amyl	4-ethenylphenyl	phenyl	
tert-amyl	tert-amyl	2-biphenylyl	phenyl	
tert-amyl	tert-amyl	3-biphenylyl	phenyl	
tert-amyl	tert-amyl	4-biphenylyl	phenyl	
tert-amyl	tert-amyl	1-naphthyl	phenyl	
tert-amyl	tert-amyl	2-naphthyl	phenyl	
tert-amyl	tert-amyl	1,1'-binaphthalene-2-yl	phenyl	
tert-amyl	tert-amyl	2-methoxyphenyl	phenyl	
tert-amyl	tert-amyl	3-methoxyphenyl	phenyl	
tert-amyl	tert-amyl	4-methoxyphenyl	phenyl	
tert-amyl	tert-amyl	2-tert-butoxyphenyl	phenyl	
tert-amyl	tert-amyl	3-tert-butoxyphenyl	phenyl	
tert-amyl	tert-amyl	4-tert-butoxyphenyl	phenyl	
tert-amyl	tert-amyl	2-dimethylaminophenyl	phenyl	

[0147] [Table 12-3]

Table 12-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-amyl	tert-amyl	3-dimethylaminophenyl	phenyl	
tert-amyl	tert-amyl	4-dimethylaminophenyl	phenyl	
tert-amyl	tert-amyl	2′-dimethylamino-2-biphenylyl	phenyl	
tert-amyl	tert-amyl	8-dimethylamino-1-naphthyl	phenyl	
tert-amyl	tert-amyl	2′-dimethylamino-1,1′-binaphthalene-2-yl	phenyl	
tert-amyl	tert-amyl	benzyl	phenyl	
tert-amyl	tert-amyl	1-phenylethyl	phenyl	
tert-amyl	tert-amyl	2-phenylethyl	phenyl	
tert-amyl	tert-amyl	2-ethenylbenzyl	phenyl	
tert-amyl	tert-amyl	3-ethenylbenzyl	phenyl	
tert-amyl	tert-amyl	4-ethenylbenzyl	phenyl	
tert-amyl	tert-amyl	4-(2-ethenylphenyl)butyl	phenyl	
tert-amyl	tert-amyl	4-(3-ethenylphenyl)butyl	phenyl	
tert-amyl	tert-amyl	4-(4-ethenylphenyl)butyl	phenyl	
tert-amyl	tert-amyl	vinyl	phenyl	
tert-amyl	tert-amyl	methallyl	phenyl	
tert-amyl	tert-amyl	1-octenyl	phenyl	
tert-amyl	tert-amyl	ethynyl	phenyl	
tert-amyl	tert-amyl	1-propynyl	phenyl	
tert-amyl	tert-amyl	1-octynyl	phenyl	
tert-amyl	tert-amyl	allyl	phenyl	
tert-amyl	tert-amyl	2-octenyl	phenyl	

[0148] [Table 13-1]

Table 13-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
1-adamantyl	1-adamantyl	hydrogen	phenyl	
1-adamantyl	1-adamantyl	methyl	phenyl	
1-adamantyl	1-adamantyl	ethyl	phenyl	
1-adamantyl	1-adamantyl	n-propyl	phenyl	
1-adamantyl	1-adamantyl	n-butyl	phenyl	
1-adamantyl	1-adamantyl	isobutyl	phenyl	
1-adamantyl	1-adamantyl	n-pentyl	phenyl	
1-adamantyl	1-adamantyl	isopentyl	phenyl	
1-adamantyl	1-adamantyl	n-hexyl	phenyl	
1-adamantyl	1-adamantyl	2-methyl-1-pentyl	phenyl	
1-adamantyl	1-adamantyl	2,2-diethyl-1-ethyl	phenyl	
1-adamantyl	1-adamantyl	n-heptyl	phenyl	
1-adamantyl	1-adamantyl	n-octyl	phenyl	
1-adamantyl	1-adamantyl	isopropyl	phenyl	
1-adamantyl	1-adamantyl	sec-butyl	phenyl	
1-adamantyl	1-adamantyl	2-pentyl	phenyl	
1-adamantyl	1-adamantyl	3-pentyl	phenyl	
1-adamantyl	1-adamantyl	2-hexyl	phenyl	
1-adamantyl	1-adamantyl	3-hexyl	phenyl	
1-adamantyl	1-adamantyl	tert-butyl	phenyl	
1-adamantyl	1-adamantyl	tert-amyl	phenyl	
1-adamantyl	1-adamantyl	1,1-dimethylbutyl	phenyl	
1-adamantyl	1-adamantyl	3-methyl-3-pentyl	phenyl	
1-adamantyl	1-adamantyl	1,1,2-trimethylpropyl	phenyl	
1-adamantyl	1-adamantyl	1-adamantyl	phenyl	
1-adamantyl	1-adamantyl	2-methyl-1-adamantyl	phenyl	
1-adamantyl	1-adamantyl	cyclopropyl	phenyl	
1-adamantyl	1-adamantyl	cyclopentyl	phenyl	
1-adamantyl	1-adamantyl	cyclohexyl	phenyl	
1-adamantyl	1-adamantyl	1-methylcyclohexyl	phenyl	
1-adamantyl	1-adamantyl	2-methylcyclohexyl	phenyl	
1-adamantyl	1-adamantyl	2-adamantyl	phenyl	
1-adamantyl	1-adamantyl	1-methyl-2-adamantyl	phenyl	

[0149] [Table 13-2]

Table 13-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
1-adamantyl	1-adamantyl	2-methyl-2-adamantyl	phenyl	
1-adamantyl	1-adamantyl	phenyl	phenyl	
1-adamantyl	1-adamantyl	ortho-tolyl	phenyl	
1-adamantyl	1-adamantyl	meta-tolyl	phenyl	
1-adamantyl	1-adamantyl	para-tolyl	phenyl	
1-adamantyl	1-adamantyl	2,3-xylyl	phenyl	
1-adamantyl	1-adamantyl	2,4-xylyl	phenyl	
1-adamantyl	1-adamantyl	2,5-xylyl	phenyl	
1-adamantyl	1-adamantyl	2,6-xylyl	phenyl	
1-adamantyl	1-adamantyl	3,4-xylyl	phenyl	
1-adamantyl	1-adamantyl	3,5-xylyl	phenyl	
1-adamantyl	1-adamantyl	mesityl	phenyl	
1-adamantyl	1-adamantyl	2-tert-butylphenyl	phenyl	
1-adamantyl	1-adamantyl	3-tert-butylphenyl	phenyl	
1-adamantyl	1-adamantyl	4-tert-butylphenyl	phenyl	
1-adamantyl	1-adamantyl	2-ethenylphenyl	phenyl	
1-adamantyl	1-adamantyl	3-ethenylphenyl	phenyl	
1-adamantyl	1-adamantyl	4-ethenylphenyl	phenyl	
1-adamantyl	1-adamantyl	2-biphenylyl	phenyl	
1-adamantyl	1-adamantyl	3-biphenylyl	phenyl	
1-adamantyl	1-adamantyl	4-biphenylyl	phenyl	
1-adamantyl	1-adamantyl	1-naphthyl	phenyl	
1-adamantyl	1-adamantyl	2-naphthyl	phenyl	
1-adamantyl	1-adamantyl	1,1'-binaphthalene-2-yl	phenyl	
1-adamantyl	1-adamantyl	2-methoxyphenyl	phenyl	
1-adamantyl	1-adamantyl	3-methoxyphenyl	phenyl	
1-adamantyl	1-adamantyl	4-methoxyphenyl	phenyl	
1-adamantyl	1-adamantyl	2-tert-butoxyphenyl	phenyl	
1-adamantyl	1-adamantyl	3-tert-butoxyphenyl	phenyl	
1-adamantyl	1-adamantyl	4-tert-butoxyphenyl	phenyl	

[0150] [Table 13-3]

Table 13-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
1-adamantyl	1-adamantyl	2-dimethylaminophenyl	phenyl	
1-adamantyl	1-adamantyl	3-dimethylaminophenyl	phenyl	
1-adamantyl	1-adamantyl	4-dimethylaminophenyl	phenyl	
1-adamantyl	1-adamantyl	2′-dimethylamino-2-biphenylyl	phenyl	
1-adamantyl	1-adamantyl	8-dimethylamino-1-naphthyl	phenyl	
1-adamantyl	1-adamantyl	2′-dimethylamino-1,1′-binaphthalene-2-yl	phenyl	
1-adamantyl	1-adamantyl	benzyl	phenyl	
1-adamantyl	1-adamantyl	1-phenylethyl	phenyl	
1-adamantyl	1-adamantyl	2-phenylethyl	phenyl	
1-adamantyl	1-adamantyl	2-ethenylbenzyl	phenyl	
1-adamantyl	1-adamantyl	3-ethenylbenzyl	phenyl	
1-adamantyl	1-adamantyl	4-ethenylbenzyl	phenyl	
1-adamantyl	1-adamantyl	4-(2-ethenylphenyl)butyl	phenyl	
1-adamantyl	1-adamantyl	4-(3-ethenylphenyl)butyl	phenyl	
1-adamantyl	1-adamantyl	4-(4-ethenylphenyl)butyl	phenyl	
1-adamantyl	1-adamantyl	vinyl	phenyl	
1-adamantyl	1-adamantyl	methallyl	phenyl	
1-adamantyl	1-adamantyl	1-octenyl	phenyl	
1-adamantyl	1-adamantyl	ethynyl	phenyl	
1-adamantyl	1-adamantyl	1-propynyl	phenyl	
1-adamantyl	1-adamantyl	1-octynyl	phenyl	
1-adamantyl	1-adamantyl	allyl	phenyl	
1-adamantyl	1-adamantyl	2-octenyl	phenyl	

[0151] [Table 14-1]

Table 14-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
2-adamantyl	2-adamantyl	hydrogen	phenyl	
2-adamantyl	2-adamantyl	methyl	phenyl	
2-adamantyl	2-adamantyl	ethyl	phenyl	
2-adamantyl	2-adamantyl	n-propyl	phenyl	
2-adamantyl	2-adamantyl	n-butyl	phenyl	
2-adamantyl	2-adamantyl	isobutyl	phenyl	
2-adamantyl	2-adamantyl	n-pentyl	phenyl	
2-adamantyl	2-adamantyl	isopentyl	phenyl	
2-adamantyl	2-adamantyl	n-hexyl	phenyl	
2-adamantyl	2-adamantyl	2-methyl-1-pentyl	phenyl	
2-adamantyl	2-adamantyl	2,2-diethyl-1-ethyl	phenyl	
2-adamantyl	2-adamantyl	n-heptyl	phenyl	
2-adamantyl	2-adamantyl	n-octyl	phenyl	
2-adamantyl	2-adamantyl	isopropyl	phenyl	
2-adamantyl	2-adamantyl	sec-butyl	phenyl	
2-adamantyl	2-adamantyl	2-pentyl	phenyl	
2-adamantyl	2-adamantyl	3-pentyl	phenyl	
2-adamantyl	2-adamantyl	2-hexyl	phenyl	
2-adamantyl	2-adamantyl	3-hexyl	phenyl	
2-adamantyl	2-adamantyl	tert-butyl	phenyl	
2-adamantyl	2-adamantyl	tert-amyl	phenyl	
2-adamantyl	2-adamantyl	1,1-dimethylbutyl	phenyl	
2-adamantyl	2-adamantyl	3-methyl-3-pentyl	phenyl	
2-adamantyl	2-adamantyl	1,1,2-trimethylpropyl	phenyl	
2-adamantyl	2-adamantyl	1-adamantyl	phenyl	
2-adamantyl	2-adamantyl	2-methyl-1-adamantyl	phenyl	
2-adamantyl	2-adamantyl	cyclopropyl	phenyl	
2-adamantyl	2-adamantyl	cyclopentyl	phenyl	
2-adamantyl	2-adamantyl	cyclohexyl	phenyl	
2-adamantyl	2-adamantyl	1-methylcyclohexyl	phenyl	
2-adamantyl	2-adamantyl	2-methylcyclohexyl	phenyl	
2-adamantyl	2-adamantyl	2-adamantyl	phenyl	
2-adamantyl	2-adamantyl	1-methyl-2-adamantyl	phenyl	
2-adamantyl	2-adamantyl	2-methyl-2-adamantyl	phenyl	
2-adamantyl	2-adamantyl	phenyl	phenyl	

[0152] [Table 14-2]

Table 14-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
2-adamantyl	2-adamantyl	ortho-tolyl	phenyl	
2-adamantyl	2-adamantyl	meta-tolyl	phenyl	
2-adamantyl	2-adamantyl	para-tolyl	phenyl	
2-adamantyl	2-adamantyl	2,3-xylyl	phenyl	
2-adamantyl	2-adamantyl	2,4-xylyl	phenyl	
2-adamantyl	2-adamantyl	2,5-xylyl	phenyl	
2-adamantyl	2-adamantyl	2,6-xylyl	phenyl	
2-adamantyl	2-adamantyl	3,4-xylyl	phenyl	
2-adamantyl	2-adamantyl	3,5-xylyl	phenyl	
2-adamantyl	2-adamantyl	mesityl	phenyl	
2-adamantyl	2-adamantyl	2-tert-butylphenyl	phenyl	
2-adamantyl	2-adamantyl	3-tert-butylphenyl	phenyl	
2-adamantyl	2-adamantyl	4-tert-butylphenyl	phenyl	
2-adamantyl	2-adamantyl	2-ethenylphenyl	phenyl	
2-adamantyl	2-adamantyl	3-ethenylphenyl	phenyl	
2-adamantyl	2-adamantyl	4-ethenylphenyl	phenyl	
2-adamantyl	2-adamantyl	2-biphenylyl	phenyl	
2-adamantyl	2-adamantyl	3-biphenylyl	phenyl	
2-adamantyl	2-adamantyl	4-biphenylyl	phenyl	
2-adamantyl	2-adamantyl	1-naphthyl	phenyl	
2-adamantyl	2-adamantyl	2-naphthyl	phenyl	
2-adamantyl	2-adamantyl	1,1′-binaphthalene-2-yl	phenyl	
2-adamantyl	2-adamantyl	2-methoxyphenyl	phenyl	
2-adamantyl	2-adamantyl	3-methoxyphenyl	phenyl	
2-adamantyl	2-adamantyl	4-methoxyphenyl	phenyl	
2-adamantyl	2-adamantyl	2-tert-butoxyphenyl	phenyl	
2-adamantyl	2-adamantyl	3-tert-butoxyphenyl	phenyl	
2-adamantyl	2-adamantyl	4-tert-butoxyphenyl	phenyl	
2-adamantyl	2-adamantyl	2-dimethylaminophenyl	phenyl	
2-adamantyl	2-adamantyl	3-dimethylaminophenyl	phenyl	

[0153] [Table 14-3]

Table 14-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
2-adamantyl	2-adamantyl	4-dimethylaminophenyl	phenyl	
2-adamantyl	2-adamantyl	2′-dimethylamino-2-biphenylyl	phenyl	
2-adamantyl	2-adamantyl	8-dimethylamino-1-naphthyl	phenyl	
2-adamantyl	2-adamantyl	2′-dimethylamino-1,1′-binaphthalene-2-yl	phenyl	
2-adamantyl	2-adamantyl	benzyl	phenyl	
2-adamantyl	2-adamantyl	1-phenylethyl	phenyl	
2-adamantyl	2-adamantyl	2-phenylethyl	phenyl	
2-adamantyl	2-adamantyl	2-ethenylbenzyl	phenyl	
2-adamantyl	2-adamantyl	3-ethenylbenzyl	phenyl	
2-adamantyl	2-adamantyl	4-ethenylbenzyl	phenyl	
2-adamantyl	2-adamantyl	4-(2-ethenylphenyl)butyl	phenyl	
2-adamantyl	2-adamantyl	4-(3-ethenylphenyl)butyl	phenyl	
2-adamantyl	2-adamantyl	4-(4-ethenylphenyl)butyl	phenyl	
2-adamantyl	2-adamantyl	vinyl	phenyl	
2-adamantyl	2-adamantyl	methallyl	phenyl	
2-adamantyl	2-adamantyl	1-octenyl	phenyl	
2-adamantyl	2-adamantyl	ethynyl	phenyl	
2-adamantyl	2-adamantyl	1-propynyl	phenyl	
2-adamantyl	2-adamantyl	1-octynyl	phenyl	
2-adamantyl	2-adamantyl	allyl	phenyl	
2-adamantyl	2-adamantyl	2-octenyl	phenyl	

[0154] [Table 15-1]

Table 15-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-butyl	tert-butyl	hydrogen	para-tolyl	
tert-butyl	tert-butyl	methyl	para-tolyl	157-166
tert-butyl	tert-butyl	ethyl	para-tolyl	
tert-butyl	tert-butyl	n-propyl	para-tolyl	
tert-butyl	tert-butyl	n-butyl	para-tolyl	
tert-butyl	tert-butyl	isobutyl	para-tolyl	
tert-butyl	tert-butyl	n-pentyl	para-tolyl	
tert-butyl	tert-butyl	isopentyl	para-tolyl	
tert-butyl	tert-butyl	n-hexyl	para-tolyl	
tert-butyl	tert-butyl	2-methyl-1-pentyl	para-tolyl	
tert-butyl	tert-butyl	2,2-diethyl-1-ethyl	para-tolyl	
tert-butyl	tert-butyl	n-heptyl	para-tolyl	
tert-butyl	tert-butyl	n-octyl	para-tolyl	
tert-butyl	tert-butyl	isopropyl	para-tolyl	
tert-butyl	tert-butyl	sec-butyl	para-tolyl	
tert-butyl	tert-butyl	2-pentyl	para-tolyl	
tert-butyl	tert-butyl	3-pentyl	para-tolyl	
tert-butyl	tert-butyl	2-hexyl	para-tolyl	
tert-butyl	tert-butyl	3-hexyl	para-tolyl	
tert-butyl	tert-butyl	tert-butyl	para-tolyl	179-201
tert-butyl	tert-butyl	tert-amyl	para-tolyl	
tert-butyl	tert-butyl	1,1-dimethylbutyl	para-tolyl	
tert-butyl	tert-butyl	3-methyl-3-pentyl	para-tolyl	
tert-butyl	tert-butyl	1,1,2-trimethylpropyl	para-tolyl	
tert-butyl	tert-butyl	1-adamantyl	para-tolyl	
tert-butyl	tert-butyl	2-methyl-1-adamantyl	para-tolyl	
tert-butyl	tert-butyl	cyclopropyl	para-tolyl	
tert-butyl	tert-butyl	cyclopentyl	para-tolyl	
tert-butyl	tert-butyl	cyclohexyl	para-tolyl	
tert-butyl	tert-butyl	1-methylcyclohexyl	para-tolyl	
tert-butyl	tert-butyl	2-methylcyclohexyl	para-tolyl	
tert-butyl	tert-butyl	2-adamantyl	para-tolyl	
tert-butyl	tert-butyl	1-methyl-2-adamantyl	para-tolyl	
tert-butyl	tert-butyl	2-methyl-2-adamantyl	para-tolyl	
tert-butyl	tert-butyl	phenyl	para-tolyl	

[0155] [Table 15-2]

Table 15-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-butyl	tert-butyl	ortho-tolyl	para-tolyl	
tert-butyl	tert-butyl	meta-tolyl	para-tolyl	
tert-butyl	tert-butyl	para-tolyl	para-tolyl	
tert-butyl	tert-butyl	2,3-xylyl	para-tolyl	
tert-butyl	tert-butyl	2,4-xylyl	para-tolyl	
tert-butyl	tert-butyl	2,5-xylyl	para-tolyl	
tert-butyl	tert-butyl	2,6-xylyl	para-tolyl	
tert-butyl	tert-butyl	3,4-xylyl	para-tolyl	
tert-butyl	tert-butyl	3,5-xylyl	para-tolyl	
tert-butyl	tert-butyl	mesityl	para-tolyl	
tert-butyl	tert-butyl	2-tert-butylphenyl	para-tolyl	
tert-butyl	tert-butyl	3-tert-butylphenyl	para-tolyl	
tert-butyl	tert-butyl	4-tert-butylphenyl	para-tolyl	
tert-butyl	tert-butyl	2-ethenylphenyl	para-tolyl	
tert-butyl	tert-butyl	3-ethenylphenyl	para-tolyl	
tert-butyl	tert-butyl	4-ethenylphenyl	para-tolyl	
tert-butyl	tert-butyl	2-biphenylyl	para-tolyl	
tert-butyl	tert-butyl	3-biphenylyl	para-tolyl	
tert-butyl	tert-butyl	4-biphenylyl	para-tolyl	
tert-butyl	tert-butyl	1-naphthyl	para-tolyl	
tert-butyl	tert-butyl	2-naphthyl	para-tolyl	
tert-butyl	tert-butyl	1,1′-binaphthalene-2-yl	para-tolyl	
tert-butyl	tert-butyl	2-methoxyphenyl	para-tolyl	
tert-butyl	tert-butyl	3-methoxyphenyl	para-tolyl	
tert-butyl	tert-butyl	4-methoxyphenyl	para-tolyl	
tert-butyl	tert-butyl	2-tert-butoxyphenyl	para-tolyl	
tert-butyl	tert-butyl	3-tert-butoxyphenyl	para-tolyl	
tert-butyl	tert-butyl	4-tert-butoxyphenyl	para-tolyl	
tert-butyl	tert-butyl	2-dimethylaminophenyl	para-tolyl	
tert-butyl	tert-butyl	3-dimethylaminophenyl	para-tolyl	

[0156] [Table 15-3]

Table 15-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-butyl	tert-butyl	4-dimethylaminophenyl	para-tolyl	
tert-butyl	tert-butyl	2′-dimethylamino-2-biphenylyl	para-tolyl	
tert-butyl	tert-butyl	8-dimethylamino-1-naphthyl	para-tolyl	
tert-butyl	tert-butyl	2′-dimethylamino-1,1′-binaphthalene-2-yl	para-tolyl	
tert-butyl	tert-butyl	benzyl	para-tolyl	
tert-butyl	tert-butyl	1-phenylethyl	para-tolyl	
tert-butyl	tert-butyl	2-phenylethyl	para-tolyl	
tert-butyl	tert-butyl	2-ethenylbenzyl	para-tolyl	
tert-butyl	tert-butyl	3-ethenylbenzyl	para-tolyl	
tert-butyl	tert-butyl	4-ethenylbenzyl	para-tolyl	
tert-butyl	tert-butyl	4-(2-ethenylphenyl)butyl	para-tolyl	
tert-butyl	tert-butyl	4-(3-ethenylphenyl)butyl	para-tolyl	
tert-butyl	tert-butyl	4-(4-ethenylphenyl)butyl	para-tolyl	
tert-butyl	tert-butyl	vinyl	para-tolyl	
tert-butyl	tert-butyl	methallyl	para-tolyl	
tert-butyl	tert-butyl	1-octenyl	para-tolyl	
tert-butyl	tert-butyl	ethynyl	para-tolyl	
tert-butyl	tert-butyl	1-propynyl	para-tolyl	
tert-butyl	tert-butyl	1-octynyl	para-tolyl	
tert-butyl	tert-butyl	allyl	para-tolyl	
tert-butyl	tert-butyl	2-octenyl	para-tolyl	
isopropyl	isopropyl	isopropyl	para-tolyl	
cyclohexyl	cyclohexyl	cyclohexyl	para-tolyl	129-131

[0157] [Table 16-1]

Table 16-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-amyl	tert-amyl	hydrogen	para-tolyl	
tert-amyl	tert-amyl	methyl	para-tolyl	
tert-amyl	tert-amyl	ethyl	para-tolyl	
tert-amyl	tert-amyl	n-propyl	para-tolyl	
tert-amyl	tert-amyl	n-butyl	para-tolyl	
tert-amyl	tert-amyl	isobutyl	para-tolyl	
tert-amyl	tert-amyl	n-pentyl	para-tolyl	
tert-amyl	tert-amyl	isopentyl	para-tolyl	
tert-amyl	tert-amyl	n-hexyl	para-tolyl	
tert-amyl	tert-amyl	2-methyl-1-pentyl	para-tolyl	
tert-amyl	tert-amyl	2,2-diethyl-1-ethyl	para-tolyl	
tert-amyl	tert-amyl	n-heptyl	para-tolyl	
tert-amyl	tert-amyl	n-octyl	para-tolyl	
tert-amyl	tert-amyl	isopropyl	para-tolyl	
tert-amyl	tert-amyl	sec-butyl	para-tolyl	
tert-amyl	tert-amyl	2-pentyl	para-tolyl	
tert-amyl	tert-amyl	3-pentyl	para-tolyl	
tert-amyl	tert-amyl	2-hexyl	para-tolyl	
tert-amyl	tert-amyl	3-hexyl	para-tolyl	
tert-amyl	tert-amyl	tert-butyl	para-tolyl	
tert-amyl	tert-amyl	tert-amyl	para-tolyl	
tert-amyl	tert-amyl	1,1-dimethylbutyl	para-tolyl	
tert-amyl	tert-amyl	3-methyl-3-pentyl	para-tolyl	
tert-amyl	tert-amyl	1,1,2-trimethylpropyl	para-tolyl	
tert-amyl	tert-amyl	1-adamantyl	para-tolyl	
tert-amyl	tert-amyl	2-methyl-1-adamantyl	para-tolyl	
tert-amyl	tert-amyl	cyclopropyl	para-tolyl	
tert-amyl	tert-amyl	cyclopentyl	para-tolyl	
tert-amyl	tert-amyl	cyclohexyl	para-tolyl	
tert-amyl	tert-amyl	1-methylcyclohexyl	para-tolyl	
tert-amyl	tert-amyl	2-methylcyclohexyl	para-tolyl	
tert-amyl	tert-amyl	2-adamantyl	para-tolyl	
tert-amyl	tert-amyl	1-methyl-2-adamantyl	para-tolyl	
tert-amyl	tert-amyl	2-methyl-2-adamantyl	para-tolyl	
tert-amyl	tert-amyl	phenyl	para-tolyl	

[0158] [Table 16-2]

Table 16-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-amyl	tert-amyl	ortho-tolyl	para-tolyl	
tert-amyl	tert-amyl	meta-tolyl	para-tolyl	
tert-amyl	tert-amyl	para-tolyl	para-tolyl	
tert-amyl	tert-amyl	2,3-xylyl	para-tolyl	
tert-amyl	tert-amyl	2,4-xylyl	para-tolyl	
tert-amyl	tert-amyl	2,5-xylyl	para-tolyl	
tert-amyl	tert-amyl	2,6-xylyl	para-tolyl	
tert-amyl	tert-amyl	3,4-xylyl	para-tolyl	
tert-amyl	tert-amyl	3,5-xylyl	para-tolyl	
tert-amyl	tert-amyl	mesityl	para-tolyl	
tert-amyl	tert-amyl	2-tert-butylphenyl	para-tolyl	
tert-amyl	tert-amyl	3-tert-butylphenyl	para-tolyl	
tert-amyl	tert-amyl	4-tert-butylphenyl	para-tolyl	
tert-amyl	tert-amyl	2-ethenylphenyl	para-tolyl	
tert-amyl	tert-amyl	3-ethenylphenyl	para-tolyl	
tert-amyl	tert-amyl	4-ethenylphenyl	para-tolyl	
tert-amyl	tert-amyl	2-biphenylyl	para-tolyl	
tert-amyl	tert-amyl	3-biphenylyl	para-tolyl	
tert-amyl	tert-amyl	4-biphenylyl	para-tolyl	
tert-amyl	tert-amyl	1-naphthyl	para-tolyl	
tert-amyl	tert-amyl	2-naphthyl	para-tolyl	
tert-amyl	tert-amyl	1,1'-binaphthalene-2-yl	para-tolyl	
tert-amyl	tert-amyl	2-methoxyphenyl	para-tolyl	
tert-amyl	tert-amyl	3-methoxyphenyl	para-tolyl	
tert-amyl	tert-amyl	4-methoxyphenyl	para-tolyl	
tert-amyl	tert-amyl	2-tert-butoxyphenyl	para-tolyl	
tert-amyl	tert-amyl	3-tert-butoxyphenyl	para-tolyl	
tert-amyl	tert-amyl	4-tert-butoxyphenyl	para-tolyl	
tert-amyl	tert-amyl	2-dimethylaminophenyl	para-tolyl	
tert-amyl	tert-amyl	3-dimethylaminophenyl	para-tolyl	

[0159] [Table 16-3]

Table 16-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
tert-amyl	tert-amyl	4-dimethylaminophenyl	para-tolyl	
tert-amyl	tert-amyl	2'-dimethylamino-2-biphenylyl	para-tolyl	
tert-amyl	tert-amyl	8-dimethylamino-1-naphthyl	para-tolyl	
tert-amyl	tert-amyl	2'-dimethylamino-1,1'-binaphthalene-2-yl	para-tolyl	
tert-amyl	tert-amyl	benzyl	para-tolyl	
tert-amyl	tert-amyl	1-phenylethyl	para-tolyl	
tert-amyl	tert-amyl	2-phenylethyl	para-tolyl	
tert-amyl	tert-amyl	2-ethenylbenzyl	para-tolyl	
tert-amyl	tert-amyl	3-ethenylbenzyl	para-tolyl	
tert-amyl	tert-amyl	4-ethenylbenzyl	para-tolyl	
tert-amyl	tert-amyl	4-(2-ethenylphenyl)butyl	para-tolyl	
tert-amyl	tert-amyl	4-(3-ethenylphenyl)butyl	para-tolyl	
tert-amyl	tert-amyl	4-(4-ethenylphenyl)butyl	para-tolyl	
tert-amyl	tert-amyl	vinyl	para-tolyl	
tert-amyl	tert-amyl	methallyl	para-tolyl	
tert-amyl	tert-amyl	1-octenyl	para-tolyl	
tert-amyl	tert-amyl	ethynyl	para-tolyl	
tert-amyl	tert-amyl	1-propynyl	para-tolyl	
tert-amyl	tert-amyl	1-octynyl	para-tolyl	
tert-amyl	tert-amyl	allyl	para-tolyl	
tert-amyl	tert-amyl	2-octenyl	para-tolyl	

[0160] [Table 17-1]

Table 17-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
1-adamantyl	1-adamantyl	hydrogen	para-tolyl	
1-adamantyl	1-adamantyl	methyl	para-tolyl	
1-adamantyl	1-adamantyl	ethyl	para-tolyl	
1-adamantyl	1-adamantyl	n-propyl	para-tolyl	
1-adamantyl	1-adamantyl	n-butyl	para-tolyl	
1-adamantyl	1-adamantyl	isobutyl	para-tolyl	
1-adamantyl	1-adamantyl	n-pentyl	para-tolyl	
1-adamantyl	1-adamantyl	isopentyl	para-tolyl	
1-adamantyl	1-adamantyl	n-hexyl	para-tolyl	
1-adamantyl	1-adamantyl	2-methyl-1-pentyl	para-tolyl	
1-adamantyl	1-adamantyl	2,2-diethyl-1-ethyl	para-tolyl	
1-adamantyl	1-adamantyl	n-heptyl	para-tolyl	
1-adamantyl	1-adamantyl	n-octyl	para-tolyl	
1-adamantyl	1-adamantyl	isopropyl	para-tolyl	
1-adamantyl	1-adamantyl	sec-butyl	para-tolyl	
1-adamantyl	1-adamantyl	2-pentyl	para-tolyl	
1-adamantyl	1-adamantyl	3-pentyl	para-tolyl	
1-adamantyl	1-adamantyl	2-hexyl	para-tolyl	
1-adamantyl	1-adamantyl	3-hexyl	para-tolyl	
1-adamantyl	1-adamantyl	tert-butyl	para-tolyl	
1-adamantyl	1-adamantyl	tert-amyl	para-tolyl	
1-adamantyl	1-adamantyl	1,1-dimethylbutyl	para-tolyl	
1-adamantyl	1-adamantyl	3-methyl-3-pentyl	para-tolyl	
1-adamantyl	1-adamantyl	1,1,2-trimethylpropyl	para-tolyl	
1-adamantyl	1-adamantyl	1-adamantyl	para-tolyl	
1-adamantyl	1-adamantyl	2-methyl-1-adamantyl	para-tolyl	
1-adamantyl	1-adamantyl	cyclopropyl	para-tolyl	
1-adamantyl	1-adamantyl	cyclopentyl	para-tolyl	
1-adamantyl	1-adamantyl	cyclohexyl	para-tolyl	
1-adamantyl	1-adamantyl	1-methylcyclohexyl	para-tolyl	
1-adamantyl	1-adamantyl	2-methylcyclohexyl	para-tolyl	
1-adamantyl	1-adamantyl	2-adamantyl	para-tolyl	
1-adamantyl	1-adamantyl	1-methyl-2-adamantyl	para-tolyl	
1-adamantyl	1-adamantyl	2-methyl-2-adamantyl	para-tolyl	
1-adamantyl	1-adamantyl	phenyl	para-tolyl	

[0161] [Table 17-2]

Table 17-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
1-adamantyl	1-adamantyl	ortho-tolyl	para-tolyl	
1-adamantyl	1-adamantyl	meta-tolyl	para-tolyl	
1-adamantyl	1-adamantyl	para-tolyl	para-tolyl	
1-adamantyl	1-adamantyl	2,3-xylyl	para-tolyl	
1-adamantyl	1-adamantyl	2,4-xylyl	para-tolyl	
1-adamantyl	1-adamantyl	2,5-xylyl	para-tolyl	
1-adamantyl	1-adamantyl	2,6-xylyl	para-tolyl	
1-adamantyl	1-adamantyl	3,4-xylyl	para-tolyl	
1-adamantyl	1-adamantyl	3,5-xylyl	para-tolyl	
1-adamantyl	1-adamantyl	mesityl	para-tolyl	
1-adamantyl	1-adamantyl	2-tert-butylphenyl	para-tolyl	
1-adamantyl	1-adamantyl	3-tert-butylphenyl	para-tolyl	
1-adamantyl	1-adamantyl	4-tert-butylphenyl	para-tolyl	
1-adamantyl	1-adamantyl	2-ethenylphenyl	para-tolyl	
1-adamantyl	1-adamantyl	3-ethenylphenyl	para-tolyl	
1-adamantyl	1-adamantyl	4-ethenylphenyl	para-tolyl	
1-adamantyl	1-adamantyl	2-biphenylyl	para-tolyl	
1-adamantyl	1-adamantyl	3-biphenylyl	para-tolyl	
1-adamantyl	1-adamantyl	4-biphenylyl	para-tolyl	
1-adamantyl	1-adamantyl	1-naphthyl	para-tolyl	
1-adamantyl	1-adamantyl	2-naphthyl	para-tolyl	
1-adamantyl	1-adamantyl	1,1′-binaphthalene-2-yl	para-tolyl	
1-adamantyl	1-adamantyl	2-methoxyphenyl	para-tolyl	
1-adamantyl	1-adamantyl	3-methoxyphenyl	para-tolyl	
1-adamantyl	1-adamantyl	4-methoxyphenyl	para-tolyl	
1-adamantyl	1-adamantyl	2-tert-butoxyphenyl	para-tolyl	
1-adamantyl	1-adamantyl	3-tert-butoxyphenyl	para-tolyl	
1-adamantyl	1-adamantyl	4-tert-butoxyphenyl	para-tolyl	
1-adamantyl	1-adamantyl	2-dimethylaminophenyl	para-tolyl	
1-adamantyl	1-adamantyl	3-dimethylaminophenyl	para-tolyl	

[0162] [Table 17-3]

Table 17-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
1-adamantyl	1-adamantyl	4-dimethylaminophenyl	para-tolyl	
1-adamantyl	1-adamantyl	2'-dimethylamino-2-biphenylyl	para-tolyl	
1-adamantyl	1-adamantyl	8-dimethylamino-1-naphthyl	para-tolyl	
1-adamantyl	1-adamantyl	2'-dimethylamino-1,1'-binaphthalene-2-yl	para-tolyl	
1-adamantyl	1-adamantyl	benzyl	para-tolyl	
1-adamantyl	1-adamantyl	1-phenylethyl	para-tolyl	
1-adamantyl	1-adamantyl	2-phenylethyl	para-tolyl	
1-adamantyl	1-adamantyl	2-ethenylbenzyl	para-tolyl	
1-adamantyl	1-adamantyl	3-ethenylbenzyl	para-tolyl	
1-adamantyl	1-adamantyl	4-ethenylbenzyl	para-tolyl	
1-adamantyl	1-adamantyl	4-(2-ethenylphenyl)butyl	para-tolyl	
1-adamantyl	1-adamantyl	4-(3-ethenylphenyl)butyl	para-tolyl	
1-adamantyl	1-adamantyl	4-(4-ethenylphenyl)butyl	para-tolyl	
1-adamantyl	1-adamantyl	vinyl	para-tolyl	
1-adamantyl	1-adamantyl	methallyl	para-tolyl	
1-adamantyl	1-adamantyl	1-octenyl	para-tolyl	
1-adamantyl	1-adamantyl	ethynyl	para-tolyl	
1-adamantyl	1-adamantyl	1-propynyl	para-tolyl	
1-adamantyl	1-adamantyl	1-octynyl	para-tolyl	
1-adamantyl	1-adamantyl	allyl	para-tolyl	
1-adamantyl	1-adamantyl	2-octenyl	para-tolyl	

[0163] [Table 18-1]

Table 18-1

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
2-adamantyl	2-adamantyl	hydrogen	para-tolyl	
2-adamantyl	2-adamantyl	methyl	para-tolyl	
2-adamantyl	2-adamantyl	ethyl	para-tolyl	
2-adamantyl	2-adamantyl	n-propyl	para-tolyl	
2-adamantyl	2-adamantyl	n-butyl	para-tolyl	
2-adamantyl	2-adamantyl	isobutyl	para-tolyl	
2-adamantyl	2-adamantyl	n-pentyl	para-tolyl	
2-adamantyl	2-adamantyl	isopentyl	para-tolyl	
2-adamantyl	2-adamantyl	n-hexyl	para-tolyl	
2-adamantyl	2-adamantyl	2-methyl-1-pentyl	para-tolyl	
2-adamantyl	2-adamantyl	2,2-diethyl-1-ethyl	para-tolyl	
2-adamantyl	2-adamantyl	n-heptyl	para-tolyl	
2-adamantyl	2-adamantyl	n-octyl	para-tolyl	
2-adamantyl	2-adamantyl	isopropyl	para-tolyl	
2-adamantyl	2-adamantyl	sec-butyl	para-tolyl	
2-adamantyl	2-adamantyl	2-pentyl	para-tolyl	
2-adamantyl	2-adamantyl	3-pentyl	para-tolyl	
2-adamantyl	2-adamantyl	2-hexyl	para-tolyl	
2-adamantyl	2-adamantyl	3-hexyl	para-tolyl	
2-adamantyl	2-adamantyl	tert-butyl	para-tolyl	
2-adamantyl	2-adamantyl	tert-amyl	para-tolyl	
2-adamantyl	2-adamantyl	1,1-dimethylbutyl	para-tolyl	
2-adamantyl	2-adamantyl	3-methyl-3-pentyl	para-tolyl	
2-adamantyl	2-adamantyl	1,1,2-trimethylpropyl	para-tolyl	
2-adamantyl	2-adamantyl	1-adamantyl	para-tolyl	
2-adamantyl	2-adamantyl	2-methyl-1-adamantyl	para-tolyl	
2-adamantyl	2-adamantyl	cyclopropyl	para-tolyl	
2-adamantyl	2-adamantyl	cyclopentyl	para-tolyl	
2-adamantyl	2-adamantyl	cyclohexyl	para-tolyl	
2-adamantyl	2-adamantyl	1-methylcyclohexyl	para-tolyl	
2-adamantyl	2-adamantyl	2-methylcyclohexyl	para-tolyl	
2-adamantyl	2-adamantyl	2-adamantyl	para-tolyl	
2-adamantyl	2-adamantyl	1-methyl-2-adamantyl	para-tolyl	
2-adamantyl	2-adamantyl	2-methyl-2-adamantyl	para-tolyl	
2-adamantyl	2-adamantyl	phenyl	para-tolyl	

[0164] [Table 18-2]

Table 18-2

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
2-adamantyl	2-adamantyl	ortho-tolyl	para-tolyl	
2-adamantyl	2-adamantyl	meta-tolyl	para-tolyl	
2-adamantyl	2-adamantyl	para-tolyl	para-tolyl	
2-adamantyl	2-adamantyl	2,3-xylyl	para-tolyl	
2-adamantyl	2-adamantyl	2,4-xylyl	para-tolyl	
2-adamantyl	2-adamantyl	2,5-xylyl	para-tolyl	
2-adamantyl	2-adamantyl	2,6-xylyl	para-tolyl	
2-adamantyl	2-adamantyl	3,4-xylyl	para-tolyl	
2-adamantyl	2-adamantyl	3,5-xylyl	para-tolyl	
2-adamantyl	2-adamantyl	mesityl	para-tolyl	
2-adamantyl	2-adamantyl	2-tert-butylphenyl	para-tolyl	
2-adamantyl	2-adamantyl	3-tert-butylphenyl	para-tolyl	
2-adamantyl	2-adamantyl	4-tert-butylphenyl	para-tolyl	
2-adamantyl	2-adamantyl	2-ethenylphenyl	para-tolyl	
2-adamantyl	2-adamantyl	3-ethenylphenyl	para-tolyl	
2-adamantyl	2-adamantyl	4-ethenylphenyl	para-tolyl	
2-adamantyl	2-adamantyl	2-biphenylyl	para-tolyl	
2-adamantyl	2-adamantyl	3-biphenylyl	para-tolyl	
2-adamantyl	2-adamantyl	4-biphenylyl	para-tolyl	
2-adamantyl	2-adamantyl	1-naphthyl	para-tolyl	
2-adamantyl	2-adamantyl	2-naphthyl	para-tolyl	
2-adamantyl	2-adamantyl	1,1′-binaphthalene-2-yl	para-tolyl	
2-adamantyl	2-adamantyl	2-methoxyphenyl	para-tolyl	
2-adamantyl	2-adamantyl	3-methoxyphenyl	para-tolyl	
2-adamantyl	2-adamantyl	4-methoxyphenyl	para-tolyl	
2-adamantyl	2-adamantyl	2-tert-butoxyphenyl	para-tolyl	
2-adamantyl	2-adamantyl	3-tert-butoxyphenyl	para-tolyl	
2-adamantyl	2-adamantyl	4-tert-butoxyphenyl	para-tolyl	
2-adamantyl	2-adamantyl	2-dimethylaminophenyl	para-tolyl	
2-adamantyl	2-adamantyl	3-dimethylaminophenyl	para-tolyl	

[0165] [Table 18-3]

Table 18-3

R^1	R^2	R^3	Ar	Melting point (°C) (Decomp. temp.)
2-adamantyl	2-adamantyl	4-dimethylaminophenyl	para-tolyl	
2-adamantyl	2-adamantyl	2′-dimethylamino-2-biphenylyl	para-tolyl	
2-adamantyl	2-adamantyl	8-dimethylamino-1-naphthyl	para-tolyl	
2-adamantyl	2-adamantyl	2′-dimethylamino-1,1′-binaphthalene-2-yl	para-tolyl	
2-adamantyl	2-adamantyl	benzyl	para-tolyl	
2-adamantyl	2-adamantyl	1-phenylethyl	para-tolyl	
2-adamantyl	2-adamantyl	2-phenylethyl	para-tolyl	
2-adamantyl	2-adamantyl	2-ethenylbenzyl	para-tolyl	
2-adamantyl	2-adamantyl	3-ethenylbenzyl	para-tolyl	
2-adamantyl	2-adamantyl	4-ethenylbenzyl	para-tolyl	
2-adamantyl	2-adamantyl	4-(2-ethenylphenyl)butyl	para-tolyl	
2-adamantyl	2-adamantyl	4-(3-ethenylphenyl)butyl	para-tolyl	
2-adamantyl	2-adamantyl	4-(4-ethenylphenyl)butyl	para-tolyl	
2-adamantyl	2-adamantyl	vinyl	para-tolyl	
2-adamantyl	2-adamantyl	methallyl	para-tolyl	
2-adamantyl	2-adamantyl	1-octenyl	para-tolyl	
2-adamantyl	2-adamantyl	ethynyl	para-tolyl	
2-adamantyl	2-adamantyl	1-propynyl	para-tolyl	
2-adamantyl	2-adamantyl	1-octynyl	para-tolyl	
2-adamantyl	2-adamantyl	allyl	para-tolyl	
2-adamantyl	2-adamantyl	2-octenyl	para-tolyl	

[0166]

[Examples]

The present invention will be described with reference to the following examples, but it should be construed that the invention is in no way limited to the examples.

[Example 1]

[0167]

Production of di-tert-butylmethylphosphonium tetraphenylborate

A 30-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. 6.4 g (40 mmol) of di-tert-butylmethylphosphine and 6.4 ml of heptane were weighed in the flask, followed by stirring to dissolve di-tert-butylmethylphosphine. While the stirring was continuously carried out, 8.0 ml (40 mmol) of 5N hydrochloric acid was added to the solution, and the mixture was stirred at 25°C for 1 hour. Thereafter, the organic phase was analyzed by gas chromatography, which confirmed the disappearance of di-tert-butylmethylphosphine. After the completion of the reaction, the liquid was separated. The aqueous phase was washed with 6.4 ml of heptane. The aqueous phase was assumed to contain di-tert-butylmethylphosphine hydrochloride dissolved therein.

[0168]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 15.1 g (44 mmol) of sodium tetraphenylborate and 60 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously

carried out, the aqueous solution of di-tert-butylmethylphosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 17.1 g of objective di-tert-butylmethylphosphonium tetraphenylborate as white crystal. The yield (mol%) was 89% based on di-tert-butylmethylphosphine.

[0169]

The crystal was analyzed by the methods indicated below and was identified to be di-tert-butylmethylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 192-196°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.33 ppm (d, 18H, J=16.7 Hz, $\underline{H_3}C$-C-P)

1.83 ppm (d, 3H, J=13.6 Hz, $\underline{H_3}C$-P)

5.27-7.18 ppm (brd, 1H, $\underline{H}$-P)

6.80 ppm (t, 4H, J=7.15 Hz, $\underline{Ph}$-B)

6.93 ppm (t, 8H, J=7.34 Hz, $\underline{Ph}$-B)

7.20 ppm (brs, 8H, $\underline{Ph}$-B)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

-3.2 ppm (d, J=43.5 Hz, $H_3\underline{C}$-P)

26.0 ppm (s, $H_3\underline{C}$-C-P)

30.8 ppm (d, J=37.9 Hz, H_3C-$\underline{C}$-P)

121.4 ppm (s, $\underline{Ph}$-B)

125.2 ppm (dd, J=2.5 Hz, 5.6 Hz, $\underline{Ph}$-B)

135.5 ppm (d, J=1.9 Hz, $\underline{Ph}$-B)

163.3 ppm (dd, J=49.4 Hz, 98.5 Hz, $\underline{Ph}$ quaternary-B)

[Example 2]

[0170]

Production of di-tert-butylmethylphosphonium tetra-para-tolylborate

A 30-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. 6.4 g (40 mmol) of di-tert-butylmethylphosphine and 6.4 ml of heptane were weighed in the flask, followed by stirring to dissolve di-tert-butylmethylphosphine. While the stirring was continuously carried out, 11.0 ml (22 mmol) of 4N sulfuric acid was added to the solution, and the mixture

was stirred at 25°C for 1 hour. Thereafter, the organic phase was analyzed by gas chromatography, which confirmed the disappearance of di-tert-butylmethylphosphine. After the completion of the reaction, the liquid was separated. The aqueous phase was washed with 6.4 ml of heptane. The aqueous phase was assumed to contain di-tert-butylmethylphosphine sulfate dissolved therein.

[0171]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 19.1 g (48 mmol) of sodium tetra-para-tolylborate, 100 ml of tetrahydrofuran and 100 ml of toluene were weighed in the flask, followed by stirring to dissolve sodium tetra-para-tolylborate. While the stirring was continuously carried out, the aqueous solution of di-tert-butylmethylphosphine sulfate previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off and washed with 200 ml of toluene. The so obtained crystal was suspended in 200 ml of water at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 200 ml of water. The crystal was then suspended in 200 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 200 ml of methanol.

The crystal obtained was dried to give 17.2 g of objective di-tert-butylmethylphosphonium tetra-para-tolylborate as white crystal. The yield (mol%) was 80% based on di-tert-butylmethylphosphine.

[0172]

The crystal was analyzed by the methods indicated below and was identified to be di-tert-butylmethylphosphonium tetra-para-tolylborate. The analytical values and properties were as follows.

(1) Melting point: 157-166°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.32 ppm (d, 18H, J=16.5 Hz, $\underline{H_3}C-C-P$)

1.81 ppm (d, 3H, J=13.6 Hz, $\underline{H_3}C-P$)

2.15 ppm (s, 12H, $\underline{H_3}C-C_6H_4-B$)

5.18-7.08 ppm (brd, 1H, $\underline{H}-P$)

6.72 ppm (t, 8H, J=7.70 Hz, $H_3C-C_6\underline{H_4}-B$)

7.05 ppm (brs, 8H, $H_3C-C_6\underline{H_4}-B$)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

3.2 ppm (d, J=45.4 Hz, $H_3\underline{C}-P$)

20.8 ppm (s, $H_3\underline{C}-C_6H_4-B$)

26.1 ppm (s, $H_3\underline{C}-C-P$)

30.8 ppm (d, J=37.9 Hz, $H_3C-\underline{C}-P$)

126.0 ppm (dd, J=2.5 Hz, 5.6 Hz, $H_3C-\underline{C_6}H_4-B$)

129.0 ppm (s, H_3C-$\underline{C}_6H_4$ quaternary-B)

135.5 ppm (d, J=1.2 Hz, H_3C-$\underline{C}_6H_4$-B)

160.2 ppm (dd, J=49.7 Hz, 98.8 Hz, H_3C-$\underline{C}_6H_4$ quaternary-B)

[Example 3]

[0173]

Production of tri-tert-butylphosphonium tetra-para-tolylborate

The procedures in Example 2 were repeated except that 6.4 g (40 mmol) of di-tert-butylmethylphosphine was replaced with 8.1 g (40 mmol) of tri-tert-butylphosphine. Consequently, 19.0 g of objective tri-tert-butylphosphonium tetra-para-tolylborate was obtained as white crystal. The yield (mol%) was 82% based on tri-tert-butylphosphine.

[0174]

The crystal was analyzed by the methods indicated below and was identified to be tri-tert-butylphosphonium tetra-para-tolylborate. The analytical values and properties were as follows.

(1) Melting point: 179-201°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.49 ppm (d, 27H, J=15.2 Hz, $\underline{H}_3C$-C-P)

2.15 ppm (s, 12H, $\underline{H}_3C$-C_6H_4-B)

5.23-7.07 ppm (brd, 1H, $\underline{H}$-P)

6.72 ppm (t, 8H, J=7.70 Hz, $H_3C-C_6\underline{H}_4-B$)

7.05 ppm (brs, 8H, $H_3C-C_6\underline{H}_4-B$)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

20.8 ppm (s, $H_3\underline{C}-C_6H_4-B$)

29.3 ppm (s, $H_3\underline{C}-C-P$)

36.3 ppm (d, J=28.6 Hz, $H_3C-\underline{C}-P$)

125.9 ppm (dd, J=2.5 Hz, 5.6 Hz, $H_3C-\underline{C}_6H_4-B$)

129.0 ppm (s, $H_3C-\underline{C}_6H_4$ quaternary-B)

135.5 ppm (s, $H_3C-\underline{C}_6H_4-B$)

160.2 ppm (dd, J=49.7 Hz, 99.4 Hz, $H_3C-\underline{C}_6H_4$ quaternary-B)

[Example 4]

[0175]

Production of di-tert-butylethylphosphonium tetraphenylborate

The procedures in Example 1 were repeated except that 6.4 g (40 mmol) of di-tert-butylmethylphosphine was replaced with 7.0 g (40 mmol) of di-tert-butylethylphosphine. Consequently, 15.8 g of objective di-tert-butylethylphosphonium tetraphenylborate was obtained as white crystal. The yield (mol%) was 80% based on di-tert-butylethylphosphine.

[0176]

The crystal was analyzed by the methods indicated below and was identified to be di-tert-butylethylphosphonium

tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 174-188°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.30 ppm (dt, 3H, J=18.7, 7.70 Hz, $\underline{H_3}C-CH_2-P$)

1.38 ppm (d, 18H, J=16.1 Hz, $\underline{H_3}C-C-P$)

2.33-2.39 ppm (m, 2H, $H_3C-C\underline{H_2}-P$)

5.92 ppm (brd, 1H, J=466.6 Hz, $\underline{H}-P$)

6.79 ppm (t, 4H, J=7.15 Hz, Ph-B)

6.93 ppm (t, 8H, J=7.34 Hz, Ph-B)

7.19 ppm (brs, 8H, Ph-B)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

7.0 ppm (d, J=41.0 Hz, $H_3C-\underline{C}H_2-P$)

11.0 ppm (d, J=6.2 Hz, $H_3\underline{C}-CH_2-P$)

26.3 ppm (s, $H_3\underline{C}-C-P$)

32.2 ppm (d, J=35.4 Hz, $H_3C-\underline{C}-P$)

121.5 ppm (s, Ph-B)

125.2 ppm (dd, J=3.1 Hz, 5.6 Hz, Ph-B)

135.5 ppm (d, J=1.2 Hz, Ph-B)

163.3 ppm (dd, J=49.5 Hz, 98.5 Hz, Ph quaternary-B)

[Example 5]

[0177]

Production of n-butyl-di-tert-butylphosphonium

tetraphenylborate

The procedures in Example 1 were repeated except that 6.4 g (40 mmol) of di-tert-butylmethylphosphine was replaced with 8.1 g (40 mmol) of n-butyl-di-tert-butylphosphine. Consequently, 15.9 g of objective n-butyl-di-tert-butylphosphonium tetraphenylborate was obtained as white crystal. The yield (mol%) was 76% based on n-butyl-di-tert-butylphosphine.

[0178]

The crystal was analyzed by the methods indicated below and was identified to be n-butyl-di-tert-butylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 156-162°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

0.93 ppm (t, 3H, J=7.34 Hz, $\underline{H_3}C-CH_2-CH_2-CH_2-P$)

1.40 ppm (d, 18H, J=16.1 Hz, $\underline{H_3}C-C-P$)

1.43-1.51 ppm (m, 2H, $H_3C-C\underline{H_2}-CH_2-CH_2-P$)

1.59-1.61 ppm (m, 2H, $H_3C-CH_2-C\underline{H_2}-CH_2-P$)

2.28-2.38 ppm (m, 2H, $H_3C-CH_2-CH_2-C\underline{H_2}-P$)

5.21-7.18 ppm (brd, 1H, $\underline{H}$-P)

6.79 ppm (t, 4H, J=7.15 Hz, $\underline{Ph}$-B)

6.92 ppm (t, 8H, J=7.34 Hz, $\underline{Ph}$-B)

7.18 ppm (brs, 8H, Ph-B)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

12.8 ppm (d, J=40.4 Hz, $H_3C-CH_2-CH_2-\underline{C}H_2-P$)

13.2 ppm (s, $H_3\underline{C}-CH_2-CH_2-CH_2-P$)

23.0 ppm (d, J=13.1 Hz, $H_3C-CH_2-\underline{C}H_2-CH_2-P$)

26.3 ppm (s, $H_3\underline{C}-C-P$)

28.5 ppm (d, J=5.6 Hz, $H_3C-\underline{C}H_2-CH_2-CH_2-P$)

32.1 ppm (d, J=35.4 Hz, $H_3C-\underline{C}-P$)

121.4 ppm (s, Ph-B)

125.2 ppm (dd, J=2.5 Hz, 5.6 Hz, Ph-B)

135.5 ppm (d, J=1.2 Hz, Ph-B)

163.4 ppm (dd, J=49.4 Hz, 98.5 Hz, Ph quaternary-B)

[Example 6]

[0179]

Production of sec-butyl-di-tert-butylphosphonium tetraphenylborate

A 100-ml four-necked flask sufficiently purged with nitrogen was equipped with a stirrer, a thermometer and a Dimroth condenser. 7.2 g (40 mmol) of di-tert-butylphosphinas chloride, 0.040 g (0.40 mmol) of copper (I) chloride and 7.2 ml of tetrahydrofuran were weighed in the flask. A sec-butylmagnesium chloride solution was added dropwise to the flask at an internal temperature of 10-20°C over a period of 1 hour, wherein the solution had been previously prepared from

4.8 g (52 mmol) of sec-butyl chloride and 1.3 g (52 mmol) of metallic magnesium in 20 g of tetrahydrofuran. The mixture was stirred at 20-30°C for 2 hours. Gas chromatography analysis confirmed the disappearance of di-tert-butylphosphinas chloride. After the completion of the reaction, 26 ml of toluene was added, and 11.8 g (6 mmol) of 5% sulfuric acid was added dropwise to dissolve the magnesium salt, followed by separation. The organic phase was washed with 11.8 ml of water.

[0180]

A 100-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. The solution of sec-butyl-di-tert-butylphosphine prepared above was weighed in the flask, to which 8.0 ml (40 mmol) of 5N hydrochloric acid was added, followed by stirring at 25°C for 1 hour. The organic phase was analyzed by gas chromatography, which confirmed the disappearance of sec-butyl-di-tert-butylphosphine. After the completion of the reaction, the liquid was separated and the aqueous phase was washed with 8.0 ml of heptane. The aqueous phase was assumed to contain sec-butyl-di-tert-butylphosphine hydrochloride dissolved therein.

[0181]

A 300-ml four-necked flask was equipped with a stirrer,

a thermometer and a Dimroth condenser. 15.1 g (44 mmol) of sodium tetraphenylborate and 60 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously carried out, the aqueous solution of sec-butyl-di-tert-butylphosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 15.7 g of objective sec-butyl-di-tert-butylphosphonium tetraphenylborate as white crystal. The yield (mol%) was 75% based on di-tert-butylphosphinas chloride.

[0182]

The crystal was analyzed by the methods indicated below and was identified to be sec-butyl-di-tert-butylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 184-187°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.03 ppm (t, 3H, J=7.34 Hz, $\underline{H}_3C-CH_2-CH-P$)

1.38-1.44 ppm (m, 3H, $\underline{H}_3C-CH-P$)

1.41 ppm (d, 9H, J=16.0 Hz, $\underline{H}_3C-C-P$)

1.45 ppm (d, 9H, J=15.8 Hz, $\underline{H}_3C-C-P$)

1.64-1.78 ppm (m, 1H, $H_3C-C\underline{H}_2-CH-P$)

1.81-1.93 ppm (m, 1H, $H_3C-C\underline{H}_2-CH-P$)

2.73-2.76 ppm (m, 1H, $H_3C-CH_2-C\underline{H}-P$)

5.22-7.19 ppm (brd, 1H, $\underline{H}-P$)

6.79 ppm (t, 4H, J=7.14 Hz, $\underline{Ph}-B$)

6.93 ppm (t, 8H, J=7.34 Hz, $\underline{Ph}-B$)

7.19 ppm (brs, 8H, $\underline{Ph}-B$)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

12.3 ppm (d, J=11.2 Hz, $H_3\underline{C}-CH-P$)

15.2 ppm (d, J=2.5 Hz, $H_3\underline{C}-CH_2-CH-P$)

26.5 ppm (s, $H_3C-\underline{C}H_2-CH-P$)

27.1 ppm (d, J=34.9 Hz, $H_3C-CH_2-\underline{C}H-P$)

27.4 ppm (s, $H_3\underline{C}-C-P$)

27.8 ppm (s, $H_3\underline{C}-C-P$)

33.8 ppm (d, J=32.3 Hz, $H_3C-\underline{C}-P$)

34.2 ppm (d, J=31.1 Hz, $H_3C-\underline{C}-P$)

121.5 ppm (s, $\underline{Ph}-B$)

125.2 ppm (dd, J=3.1 Hz, 5.6 Hz, Ph-B)

135.5 ppm (d, J=1.2 Hz, Ph-B)

163.3 ppm (dd, J=49.4 Hz, 98.5 Hz, Ph quaternary-B)

[Example 7]

[0183]

Production of cyclohexyl-di-tert-butylphosphonium tetraphenylborate

A 100-ml four-necked flask sufficiently purged with nitrogen was equipped with a stirrer, a thermometer and a Dimroth condenser. 7.2 g (40 mmol) of di-tert-butylphosphinas chloride, 0.040 g (0.40 mmol) of copper (I) chloride and 7.2 ml of tetrahydrofuran were weighed in the flask. A cyclohexylmagnesium chloride solution was added dropwise to the flask at an internal temperature of 10-20°C over a period of 1 hour, wherein the solution had been previously prepared from 6.2 g (52 mmol) of cyclohexyl chloride and 1.3 g (52 mmol) of metallic magnesium in 19 g of tetrahydrofuran. The mixture was stirred at 20-30°C for 2 hours. Gas chromatography analysis confirmed the disappearance of di-tert-butylphosphinas chloride. After the completion of the reaction, 26 ml of toluene was added, and 11.8 g (6 mmol) of 5% sulfuric acid was added dropwise to dissolve the magnesium salt, followed by separation. The organic phase was washed with 11.8 ml of water.

[0184]

A 100-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. The solution of cyclohexyl-di-tert-butylphosphine prepared above was weighed in the flask, to which 8.8 ml (44 mmol) of 5N hydrochloric acid was added, followed by stirring at 25°C for 1 hour. The organic phase was analyzed by gas chromatography, which confirmed the disappearance of cyclohexyl-di-tert-butylphosphine. After the completion of the reaction, the liquid was separated and the aqueous phase was washed with 8.8 ml of heptane. The aqueous phase was assumed to contain cyclohexyl-di-tert-butylphosphine hydrochloride dissolved therein.

[0185]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 16.4 g (48 mmol) of sodium tetraphenylborate and 66 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously carried out, the aqueous solution of cyclohexyl-di-tert-butylphosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction,

the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 15.8 g of objective cyclohexyl-di-tert-butylphosphonium tetraphenylborate as white crystal. The yield (mol%) was 72% based on di-tert-butylphosphinas chloride.

[0186]

The crystal was analyzed by the methods indicated below and was identified to be cyclohexyl-di-tert-butylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 171-178°C (decomposition temperature)

(2) IR spectrum (KBr) 2390 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.16-1.35 ppm (m, 3H, cyclohexyl secondary)

1.38 ppm (d, 18H, J=15.8 Hz, $\underline{H_3}C$-C-P)

1.62-1.75 ppm (m, 5H, cyclohexyl secondary)

1.83-2.03 ppm (m, 2H, cyclohexyl secondary)

2.60-2.72 ppm (m, 1H, cyclohexyl tertiary)

5.75 ppm (brd, 1H, J=462.3 Hz, H-P)

6.80 ppm (t, 4H, J=7.15 Hz, Ph-B)

6.94 ppm (t, 8H, J=7.34 Hz, Ph-B)

7.22 ppm (brs, 8H, Ph-B)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

24.7 ppm (d, J=1.2 Hz, cyclohexyl secondary)

26.2 ppm (d, J=11.8 Hz, cyclohexyl secondary)

27.6 ppm (s, H_3C-C-P)

28.9 ppm (d, J=3.7 Hz, cyclohexyl secondary)

30.8 ppm (d, J=34.2 Hz, cyclohexyl tertiary)

34.0 ppm (d, J=31.7 Hz, H_3C-C-P)

121.5 ppm (s, Ph-B)

125.3 ppm (dd, J=2.5 Hz, 5.6 Hz, Ph-B)

135.6 ppm (d, J=1.2 Hz, Ph-B)

163.4 ppm (dd, J=49.4 Hz, 98.5 Hz, Ph quaternary-B)

[Example 8]

[0187]

Production of di-tert-butyl-n-octylphosphonium tetraphenylborate

A 100-ml four-necked flask sufficiently purged with nitrogen was equipped with a stirrer, a thermometer and a Dimroth condenser. 7.2 g (40 mmol) of di-tert-butylphosphinas chloride, 0.040 g (0.40 mmol) of copper (I) chloride and 7.2 ml of tetrahydrofuran were weighed in the flask. A

n-octylmagnesium chloride solution was added dropwise to the flask at an internal temperature of 10-20°C over a period of 1 hour, wherein the solution had been previously prepared from 7.7 g (52 mmol) of n-octyl chloride and 1.3 g (52 mmol) of metallic magnesium in 17 g of tetrahydrofuran. The mixture was stirred at 20-30°C for 2 hours. Gas chromatography analysis confirmed the disappearance of di-tert-butylphosphinas chloride. After the completion of the reaction, 26 ml of toluene was added, and 11.8 g (6 mmol) of 5% sulfuric acid was added dropwise to dissolve the magnesium salt, followed by separation. The organic phase was washed with 11.8 ml of water.

[0188]

A 100-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. The solution of di-tert-butyl-n-octylphosphine prepared above was weighed in the flask, to which 8.8 ml (44 mmol) of 5N hydrochloric acid was added, followed by stirring at 25°C for 1 hour. The organic phase was analyzed by gas chromatography, which confirmed the disappearance of di-tert-butyl-n-octylphosphine. After the completion of the reaction, the liquid was separated and the aqueous phase was washed with 8.8 ml of heptane. The aqueous phase was assumed to contain di-tert-butyl-n-octylphosphine hydrochloride

dissolved therein.

[0189]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 16.4 g (48 mmol) of sodium tetraphenylborate and 66 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously carried out, the aqueous solution of di-tert-butyl-n-octylphosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 17.4 g of objective di-tert-butyl-n-octylphosphonium tetraphenylborate as white crystal. The yield (mol%) was 75% based on di-tert-butylphosphinas chloride.

[0190]

The crystal was analyzed by the methods indicated below

and was identified to be di-tert-butyl-n-octylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 108-113°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^1H-NMR spectrum (δ in DMSO-d6)

0.86 ppm (t, 3H, J=5.87 Hz, $\underline{H_3}C-(CH)_5-CH_2-CH_2-P$)

1.27 ppm (brs, 10H, $H_3C-(C\underline{H_2})_5-CH_2-CH_2-P$)

1.39 ppm (d, 18H, J=16.1 Hz, $\underline{H_3}C-C-P$)

1.60-1.71 ppm (m, 2H, $H_3C-(CH_2)_5-C\underline{H_2}-CH_2-P$)

2.25-2.35 ppm (m, 2H, $H_3C-(CH_2)_5-CH_2-C\underline{H_2}-P$)

5.20-7.19 ppm (brd, 1H, $\underline{H}-P$)

6.79 ppm (t, 4H, J=7.15 Hz, $\underline{Ph}-B$)

6.92 ppm (t, 8H, J=7.25 Hz, $\underline{Ph}-B$)

7.19 ppm (brs, 8H, $\underline{Ph}-B$)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

13.8 ppm (d, J=40.0 Hz, $H_3C-(CH_2)_6-\underline{C}H_2-P$)

13.9 ppm (s, $H_3\underline{C}-CH_2-CH_2-CH_2-P$)

22.0 ppm (s, $H_3C-(\underline{C}H_2)_4-(CH_2)_3-P$)

26.3 ppm (s, $H_3\underline{C}-C-P$)

26.5 ppm (d, J=6.2 Hz, $H_3C-(CH_2)_4-\underline{C}H_2-(CH_2)_2-P$)

28.2 ppm (s, $H_3C-(\underline{C}H_2)_4-(CH_2)_3-P$)

28.4 ppm (s, $H_3C-(\underline{C}H_2)_4-(CH_2)_3-P$)

29.8 ppm (d, J=11.8 Hz, $H_3C-(CH_2)_5-\underline{C}H_2-CH_2-P$)

31.1 ppm (s, $H_3C-(\underline{C}H_2)_4-(CH_2)_3-P$)

32.1 ppm (d, J=35.4 Hz, $H_3C-\underline{C}-P$)

121.4 ppm (s, Ph-B)

125.2 ppm (dd, J=2.5 Hz, 5.6 Hz, Ph-B)

135.5 ppm (d, J=1.2 Hz, Ph-B)

163.3 ppm (dd, J=49.0 Hz, 98.5 Hz, Ph quaternary-B)

[Example 9]

[0191]

Production of di-tert-butylphenylphosphonium tetraphenylborate

The procedures in Example 1 were repeated except that 6.4 g (40 mmol) of di-tert-butylmethylphosphine was replaced with 8.9 g (40 mmol) of di-tert-butylphenylphosphine. Consequently, 17.8 g of objective di-tert-butylphenylphosphonium tetraphenylborate was obtained as white crystal. The yield (mol%) was 82% based on di-tert-butylphenylphosphine.

[0192]

The crystal was analyzed by the methods indicated below and was identified to be di-tert-butylphenylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 135-140°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.40 ppm (d, 18H, J=16.7 Hz, $\underline{H_3}$C-C-P)

6.76-7.95 ppm (brd, 1H, $\underline{H}$-P)

6.79 ppm (t, 4H, J=7.15 Hz, $\underline{Ph}$-B)

6.92 ppm (t, 8H, J=7.54 Hz, $\underline{Ph}$-B)

7.19 ppm (brs, 8H, $\underline{Ph}$-B)

7.70 ppm (t, 2H, J=7.70 Hz, $\underline{Ph}$-P)

7.83 ppm (t, 1H, J=7.89 Hz, $\underline{Ph}$-P)

7.92 ppm (t, 2H, J=7.89 Hz, $\underline{Ph}$-P)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

27.0 ppm (s, $H_3\underline{C}$-C-P)

33.3 ppm (d, J=31.7 Hz, H_3C-$\underline{C}$-P)

121.5 ppm (s, $\underline{Ph}$-B)

125.3 ppm (dd, J=3.1 Hz, 5.6 Hz, $\underline{Ph}$-B)

126.6 ppm (s, $\underline{Ph}$-P)

128.3 ppm (s, $\underline{Ph}$ quaternary-P)

130.0 ppm (d, J=11.2 Hz, $\underline{Ph}$-P)

133.3 ppm (s, $\underline{Ph}$-P)

135.5 ppm (d, J=1.2 Hz, $\underline{Ph}$-B)

163.4 ppm (dd, J=49.4 Hz, 98.5 Hz, $\underline{Ph}$ quaternary-B)

[Example 10]

[0193]

Production of 2-biphenylyl-di-tert-butylphosphonium tetraphenylborate

A 50-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. 11.9 g (40 mmol) of 2-biphenylyl-di-tert-butylphosphine and 11.9 ml of heptane were weighed in the flask, followed by stirring to dissolve 2-biphenylyl-di-tert-butylphosphine. While the stirring was continuously carried out, 12.0 ml (60 mmol) of 5N hydrochloric acid was added, followed by stirring at 25°C for 1 hour. The organic phase was analyzed by gas chromatography, which confirmed the disappearance of 2-biphenylyl-di-tert-butylphosphine. After the completion of the reaction, the liquid was separated and the aqueous phase was washed with 11.9 ml of heptane. The aqueous phase was assumed to contain 2-biphenylyl-di-tert-butylphosphine hydrochloride dissolved therein.

[0194]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 22.6 g (66 mmol) of sodium tetraphenylborate and 90 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously carried out, the aqueous solution of

2-biphenylyl-di-tert-butylphosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 19.3 g of objective 2-biphenylyl-di-tert-butylphosphonium tetraphenylborate as white crystal. The yield (mol%) was 78% based on 2-biphenylyl-di-tert-butylphosphine.

[0195]

The crystal was analyzed by the methods indicated below and was identified to be 2-biphenylyl-di-tert-butylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 163-174°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.26 ppm (d, 18H, J=17.1 Hz, $\underline{H_3}C$-C-P)

6.77-7.96 ppm (brd, 1H, $\underline{H}$-P)

6.80 ppm (t, 4H, J=7.06 Hz, $\underline{\text{Ph}}$-B)

6.94 ppm (t, 8H, J=7.34 Hz, $\underline{\text{Ph}}$-B)

7.18-7.21 ppm (m, 2H, 2-biphenyl)

7.28 ppm (brs, 8H, $\underline{\text{Ph}}$-B)

7.45-7.47 ppm (m, 4H, 2-biphenyl)

7.62 ppm (d, 1H, J=7.52 Hz, 2-biphenyl)

7.72 ppm (d, 1H, J=7.61 Hz, 2-biphenyl)

7.93 ppm (d, 1H, J=8.63 Hz, 2-biphenyl)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

27.3 ppm (s, $H_3\underline{C}$-C-P)

34.2 ppm (d, J=30.5 Hz, H_3C-$\underline{C}$-P)

121.5 ppm (s, $\underline{\text{Ph}}$-B)

125.3 ppm (dd, J=2.5 Hz, 5.6 Hz, $\underline{\text{Ph}}$-B)

126.5 ppm (s, 2-biphenyl)

128.2 ppm (s, 2-biphenyl)

128.6 ppm (s, 2-biphenyl)

128.8 ppm (s, 2-biphenyl)

129.3 ppm (s, 2-biphenyl)

132.2 ppm (d, J=8.1 Hz, 2-biphenyl)

133.0 ppm (d, J=17.4 Hz, 2-biphenyl)

134.0 ppm (s, 2-biphenyl quaternary)

135.6 ppm (s, $\underline{\text{Ph}}$-B)

138.4 ppm (s, 2-biphenyl quaternary)

148.3 ppm (s, 2-biphenyl quaternary)

163.4 ppm (dd, J=49.7 Hz, 98.8 Hz, Ph quaternary-B)

[Example 11]

[0196]

Production of di-tert-butyl-1-naphthylphosphonium tetraphenylborate

The procedures in Example 10 were repeated except that 11.9 g (40 mmol) of 2-biphenylyl-di-tert-butylphosphine was replaced with 10.9 g (40 mmol) of di-tert-butyl-1-naphthylphosphine. Consequently, 19.0 g of objective di-tert-butyl-1-naphthylphosphonium tetraphenylborate was obtained as white crystal. The yield (mol%) was 80% based on di-tert-butyl-1-naphthylphosphine.

[0197]

The crystal was analyzed by the methods indicated below and was identified to be di-tert-butyl-1-naphthylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 165-174°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.39 ppm (d, 18H, J=16.9 Hz, H_3C-C-P)

6.82-8.51 ppm (brd, 1H, H-P)

6.84 ppm (t, 4H, J=7.06 Hz, Ph-B)

6.99 ppm (t, 8H, J=7.34 Hz, Ph-B)

7.35 ppm (brs, 8H, Ph-B)

7.65-7.82 ppm (m, 3H, 1-naphthyl)

8.10 ppm (d, 1H, J=8.07 Hz, 1-naphthyl)

8.13-8.19 ppm (m, 1H, 1-naphthyl)

8.32 ppm (d, 1H, J=8.25 Hz, 1-naphthyl)

8.50 ppm (d, 1H, J=8.62 Hz, 1-naphthyl)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

27.3 ppm (s, H_3<u>C</u>-C-P)

34.4 ppm (d, J=29.2 Hz, H_3C-<u>C</u>-P)

121.5 ppm (s, Ph-B)

124.1 ppm (d, J=9.9 Hz, 1-naphthyl)

125.1 ppm (s, 1-naphthyl)

125.3 ppm (dd, J=2.5 Hz, 5.6 Hz, Ph-B)

126.5 ppm (s, 1-naphthyl)

127.3 ppm (s, 1-naphthyl)

128.2 ppm (s, 1-naphthyl)

128.9 ppm (s, 1-naphthyl)

129.9 ppm (s, 1-naphthyl)

133.1 ppm (s, 1-naphthyl quaternary)

133.3 ppm (d, J=7.5 Hz, 1-naphthyl quaternary)

134.4 ppm (d, J=6.7 Hz, 1-naphthyl quaternary)

135.7 ppm (s, Ph-B)

163.5 ppm (dd, J=49.4 Hz, 98.5 Hz, Ph quaternary-B)

[Example 12]

[0198]

Production of benzyl-di-tert-butylphosphonium tetraphenylborate

The procedures in Example 1 were repeated except that 6.4 g (40 mmol) of di-tert-butylmethylphosphine was replaced with 9.5 g (40 mmol) of benzyl-di-tert-butylphosphine. Consequently, 18.0 g of objective benzyl-di-tert-butylphosphonium tetraphenylborate was obtained as white crystal. The yield (mol%) was 81% based on benzyl-di-tert-butylphosphine.

[0199]

The crystal was analyzed by the methods indicated below and was identified to be benzyl-di-tert-butylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 149-158°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.38 ppm (d, 18H, J=15.8 Hz, $\underline{H_3}$C-C-P)

3.99 ppm (brs, 2H, Ph-C$\underline{H_2}$-P)

6.76-7.44 ppm (brd, 1H, $\underline{H}$-P)

6.79 ppm (t, 4H, J=7.15 Hz, $\underline{Ph}$-B)

6.92 ppm (t, 8H, J=7.34 Hz, $\underline{Ph}$-B)

7.18 ppm (brs, 8H, $\underline{Ph}$-B)

7.32-7.44 ppm (m, 5H, $\underline{\mathrm{Ph}}\text{-CH}_2\text{-P}$)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

20.4 ppm (d, J=40.0 Hz, $\mathrm{Ph}\text{-}\underline{\mathrm{C}}\mathrm{H}_2\text{-P}$)

26.7 ppm (s, $\mathrm{H_3}\underline{\mathrm{C}}\text{-C-P}$)

32.9 ppm (d, J=32.3 Hz, $\mathrm{H_3C}\text{-}\underline{\mathrm{C}}\text{-P}$)

121.5 ppm (s, $\underline{\mathrm{Ph}}\text{-B}$)

125.2 ppm (dd, J=2.5 Hz, 5.6 Hz, $\underline{\mathrm{Ph}}\text{-B}$)

127.6 ppm (s, $\underline{\mathrm{Ph}}\text{-CH}_2\text{-P}$)

129.1 ppm (s, $\underline{\mathrm{Ph}}\text{-CH}_2\text{-P}$)

129.7 ppm (d, J=6.2 Hz, $\underline{\mathrm{Ph}}\text{-CH}_2\text{-P}$)

133.0 ppm (s, $\underline{\mathrm{Ph}}$ quaternary-$\mathrm{CH_2}$-P)

135.5 ppm (d, J=1.2 Hz, $\underline{\mathrm{Ph}}\text{-B}$)

163.3 ppm (dd, J=49.4 Hz, 98.5 Hz, $\underline{\mathrm{Ph}}$ quaternary-B)

[Example 13]

[0200]

Production of di-tert-butyl(4-ethenylbenzyl)phosphonium tetraphenylborate

A 100-ml four-necked flask sufficiently purged with nitrogen was equipped with a stirrer, a thermometer and a Dimroth condenser. 7.2 g (40 mmol) of di-tert-butylphosphinas chloride, 0.040 g (0.40 mmol) of copper (I) chloride and 7.2 ml of tetrahydrofuran were weighed in the flask. A 4-ethenylbenzylmagnesium chloride solution was added dropwise to the flask at an internal temperature of 10-20°C over a period

of 1 hour, wherein the solution had been previously prepared from 7.9 g (52 mmol) of 4-ethenylbenzyl chloride and 1.3 g (52 mmol) of metallic magnesium in 17 g of tetrahydrofuran. The mixture was stirred at 20-30°C for 2 hours. Gas chromatography analysis confirmed the disappearance of di-tert-butylphosphinas chloride. After the completion of the reaction, 26 ml of toluene was added, and 11.8 g (6 mmol) of 5% sulfuric acid was added dropwise to dissolve the magnesium salt, followed by separation. The organic phase was washed with 11.8 ml of water.

[0201]

A 100-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. The solution of di-tert-butyl(4-ethenylbenzyl)phosphine prepared above was weighed in the flask, to which 8.0 ml (40 mmol) of 5N hydrochloric acid was added, followed by stirring at 25°C for 1 hour. The organic phase was analyzed by gas chromatography, which confirmed the disappearance of di-tert-butyl(4-ethenylbenzyl)phosphine. After the completion of the reaction, the liquid was separated and the aqueous phase was washed with 8.0 ml of heptane. The aqueous phase was assumed to contain di-tert-butyl(4-ethenylbenzyl)phosphine hydrochloride

dissolved therein.

[0202]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 15.1 g (44 mmol) of sodium tetraphenylborate and 60 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously carried out, the aqueous solution of di-tert-butyl(4-ethenylbenzyl)phosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 17.7 g of objective di-tert-butyl(4-ethenylbenzyl)phosphonium tetraphenylborate as white crystal. The yield (mol%) was 76% based on di-tert-butylphosphinas chloride.

[0203]

The crystal was analyzed by the methods indicated below

and was identified to be di-tert-butyl(4-ethenylbenzyl)phosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 122-132°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.40 ppm (d, 18H, J=16.1 Hz, $\underline{H}_3C-C-P$)

3.96 ppm (brs, 2H, $H_2C=CH-C_6H_4-C\underline{H}_2-P$)

5.29 ppm (d, 1H, 11.0 Hz, $\underline{H}_2C=C\underline{H}-C_6H_4-CH_2-P$)

5.86 ppm (d, 1H, 17.8 Hz, $\underline{H}_2C=C\underline{H}-C_6H_4-CH_2-P$)

6.68-7.53 ppm (brd, 1H, $\underline{H}-P$)

6.70 ppm (d, 1H, 10.8 Hz, $\underline{H}_2C=C\underline{H}-C_6H_4-CH_2-P$)

6.78 ppm (t, 4H, J=7.15 Hz, $\underline{Ph}-B$)

6.92 ppm (t, 8H, J=7.24 Hz, $\underline{Ph}-B$)

7.18 ppm (brs, 8H, $\underline{Ph}-B$)

7.42 ppm (d, 2H, J=7.70 Hz, $H_2C=CH-C_6\underline{H}_4-CH_2-P$)

7.51 ppm (d, 2H, J=7.89 Hz, $H_2C=CH-C_6\underline{H}_4-CH_2-P$)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

20.3 ppm (d, J=34.8 Hz, $H_2C=CH-C_6H_4-\underline{C}H_2-P$)

26.7 ppm (s, $H_3\underline{C}-C-P$)

32.8 ppm (d, J=31.7 Hz, $H_3C-\underline{C}-P$)

114.9 ppm (s, $H_2\underline{C}=CH-C_6H_4-CH_2-P$)

121.5 ppm (s, $\underline{Ph}-B$)

125.2 ppm (dd, J=2.5 Hz, 5.0 Hz, Ph-B)

126.7 ppm (s, $H_2C=\underline{C}H-\underline{C}_6H_4-CH_2-P$)

128.1 ppm (d, J=6.8 Hz, $H_2C=CH-\underline{C}_6H_4$ quaternary-CH_2-P)

128.8 ppm (s, $H_2C=CH-\underline{C}_6H_4$ quaternary-CH_2-P)

129.9 ppm (s, $H_2C=\underline{C}H-\underline{C}_6H_4-CH_2-P$)

135.6 ppm (s, Ph-B)

135.8 ppm (s, $H_2C=\underline{C}H-\underline{C}_6H_4-CH_2-P$)

163.4 ppm (dd, J=49.4 Hz, 98.5 Hz, Ph quaternary-B)

[Example 14]

[0204]

Production of di-tert-butylvinylphosphonium tetraphenylborate

A 100-ml four-necked flask sufficiently purged with nitrogen was equipped with a stirrer, a thermometer and a Dimroth condenser. 7.2 g (40 mmol) of di-tert-butylphosphinas chloride, 0.040 g (0.40 mmol) of copper (I) chloride and 7.2 ml of tetrahydrofuran were weighed in the flask. A vinylmagnesium chloride solution was added dropwise to the flask at an internal temperature of 10-20°C over a period of 1 hour, wherein the solution had been previously prepared from 3.3 g (52 mmol) of vinyl chloride and 1.3 g (52 mmol) of metallic magnesium in 21 g of tetrahydrofuran. The mixture was stirred at 40-50°C for 2 hours. Gas chromatography analysis confirmed the disappearance of di-tert-butylphosphinas chloride.

After the completion of the reaction, 26 ml of toluene was added, and 11.8 g (6 mmol) of 5% sulfuric acid was added dropwise to dissolve the magnesium salt, followed by separation. The organic phase was washed with 11.8 ml of water.

[0205]

A 100-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. The solution of di-tert-butylvinylphosphine prepared above was weighed in the flask, to which 8.0 ml (40 mmol) of 5N hydrochloric acid was added, followed by stirring at 25°C for 1 hour. The organic phase was analyzed by gas chromatography, which confirmed the disappearance of di-tert-butylvinylphosphine. After the completion of the reaction, the liquid was separated and the aqueous phase was washed with 8.0 ml of heptane. The aqueous phase was assumed to contain di-tert-butylvinylphosphine hydrochloride dissolved therein.

[0206]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 15.1 g (44 mmol) of sodium tetraphenylborate and 60 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously carried out, the aqueous solution of

di-tert-butylvinylphosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 14.4 g of objective di-tert-butylvinylphosphonium tetraphenylborate as white crystal. The yield (mol%) was 73% based on di-tert-butylphosphinas chloride.

[0207]

The crystal was analyzed by the methods indicated below and was identified to be di-tert-butylvinylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 253-261°C (decomposition temperature)

(2) IR spectrum (KBr) 2359 cm^{-1}

[Example 15]

[0208]

Production of allyl-di-tert-butylphosphonium

tetraphenylborate

A 100-ml four-necked flask sufficiently purged with nitrogen was equipped with a stirrer, a thermometer and a Dimroth condenser. 7.2 g (40 mmol) of di-tert-butylphosphinas chloride, 0.040 g (0.40 mmol) of copper (I) chloride and 7.2 ml of tetrahydrofuran were weighed in the flask. An allylmagnesium chloride solution was added dropwise to the flask at an internal temperature of 10-20°C over a period of 1 hour, wherein the solution had been previously prepared from 4.0 g (52 mmol) of allyl chloride and 1.3 g (52 mmol) of metallic magnesium in 21 g of tetrahydrofuran. The mixture was stirred at 20-30°C for 1 hour. Gas chromatography analysis confirmed the disappearance of di-tert-butylphosphinas chloride. After the completion of the reaction, 26 ml of toluene was added, and 11.8 g (6 mmol) of 5% sulfuric acid was added dropwise to dissolve the magnesium salt, followed by separation. The organic phase was washed with 11.8 ml of water.

[0209]

A 200-ml four-necked flask sufficiently purged with argon was equipped with a stirrer, a thermometer and a Dimroth condenser. The solution of allyl-di-tert-butylphosphine prepared above was weighed in the flask, to which 8.0 ml (40 mmol) of 5N hydrochloric acid was added, followed by stirring at 25°C for 1 hour. The organic phase was analyzed by gas

chromatography, which confirmed the disappearance of allyl-di-tert-butylphosphine. After the completion of the reaction, the liquid was separated and the aqueous phase was washed with 8.0 ml of heptane. The aqueous phase was assumed to contain allyl-di-tert-butylphosphine hydrochloride dissolved therein.

[0210]

A 300-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 15.1 g (44 mmol) of sodium tetraphenylborate and 60 ml of water were weighed in the flask, followed by stirring to dissolve sodium tetraphenylborate. While the stirring was continuously carried out, the aqueous solution of allyl-di-tert-butylphosphine hydrochloride previously obtained was added to the solution, and the mixture was stirred at 25°C for 3 hours. After the completion of the reaction, the precipitated product was filtered off. The so obtained crystal was suspended in 100 ml of toluene at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of toluene. The crystal was then suspended in 100 ml of methanol at 50°C, and the suspension was cooled to 25°C and filtered. The product filtered off was washed with 100 ml of methanol. The crystal obtained was dried to give 15.2 g of objective

allyl-di-tert-butylphosphonium tetraphenylborate as white crystal. The yield (mol%) was 75% based on di-tert-butylphosphinas chloride.

The crystal was analyzed by the methods indicated below and was identified to be allyl-di-tert-butylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 148-160°C (decomposition temperature)

(2) IR spectrum (KBr) 2384 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.40 ppm (d, 18H, J=16.1 Hz, $\underline{H_3}C$-C-P)

3.34 ppm (brs, 2H, H_2C=CH-C$\underline{H_2}$-P)

5.33 ppm (d, 1H, 9.54 Hz, $\underline{H_2}C$=C$\underline{H}$-CH_2-P)

5.47 ppm (d, 1H, 16.3 Hz, $\underline{H_2}C$=C$\underline{H}$-CH_2-P)

5.84-5.97 ppm (m, 1H, $\underline{H_2}C$=C$\underline{H}$-CH_2-P)

6.77-7.36 ppm (brd, 1H, $\underline{H}$-P)

6.79 ppm (t, 4H, J=7.06 Hz, $\underline{Ph}$-B)

6.93 ppm (t, 8H, J=7.25 Hz, $\underline{Ph}$-B)

7.18 ppm (brs, 8H, $\underline{Ph}$-B)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

18.7 ppm (d, J=36.7 Hz, H_2C=CH-$\underline{C}H_2$-P)

26.6 ppm (s, $H_3\underline{C}$-C-P)

32.6 ppm (d, J=32.3 Hz, H_3C-$\underline{C}$-P)

109.5 ppm (s, $H_2\underline{C}$=$\underline{C}$H-CH_2-P)

115.2 ppm (s, $H_2\underline{C}=\underline{C}H-CH_2-P$)

121.5 ppm (s, <u>Ph</u>-B)

125.2 ppm (dd, J=2.5 Hz, 5.6 Hz, <u>Ph</u>-B)

135.5 ppm (s, <u>Ph</u>-B)

163.4 ppm (dd, J=49.7 Hz, 98.8 Hz, <u>Ph</u> quaternary-B)

[Example 16]

[0211]

<u>Production of tricyclohexylphosphonium tetra-para-tolylborate</u>

The procedures in Example 2 were repeated except that 6.4 g (40 mmol) of di-tert-butylmethylphosphine was replaced with 11.2 g (40 mmol) of tricyclohexylphosphine. Consequently, 22.3 g of objective tricyclohexylphosphonium tetra-para-tolylborate was obtained as white crystal. The yield (mol%) was 85% based on tricyclohexylphosphine.

[0212]

The crystal was analyzed by the methods indicated below and was identified to be tricyclohexylphosphonium tetra-para-tolylborate. The analytical values and properties were as follows.

(1) Melting point: 129-131°C

(2) IR spectrum (KBr) 2376 cm^{-1}

(3) ^1H-NMR spectrum (δ in DMSO-d6)

1.18-1.89 ppm (m, 30H, cyclohexyl secondary)

2.15 ppm (s, 12H, $\underline{H}_3C-C_6H_4-B$)

2.51-2.57 ppm (m, 3H, cyclohexyl tertiary)

5.77 ppm (brd, 1H, J=470.4 Hz, $\underline{H}$-P)

6.71 ppm (t, 8H, J=7.70 Hz, $H_3C-C_6\underline{H}_4-B$)

7.03 ppm (brs, 8H, $H_3C-C_6\underline{H}_4-B$)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

20.8 ppm (s, $H_3\underline{C}-C_6H_4-B$)

24.6 ppm (s, cyclohexyl secondary)

25.6 ppm (d, J=13.1 Hz, cyclohexyl secondary)

26.8 ppm (d, J=31.1 Hz, cyclohexyl tertiary)

27.0 ppm (s, cyclohexyl secondary)

125.9 ppm (dd, J=3.1 Hz, 5.6 Hz, $H_3C-\underline{C}_6H_4-B$)

129.0 ppm (s, $H_3C-\underline{C}_6H_4$ quaternary-B)

135.5 ppm (d, J=1.2 Hz, $H_3C-\underline{C}_6H_4-B$)

160.2 ppm (dd, J=49.4 Hz, 99.1 Hz, $H_3C-\underline{C}_6H_4$ quaternary-B)

[Example 17]

[0213]

Production of triisopropylphosphonium tetraphenylborate

The procedures in Example 1 were repeated except that 6.4 g (40 mmol) of di-tert-butylmethylphosphine was replaced with 6.4 g (40 mmol) of triisopropylphosphine. Consequently, 16.9 g of objective triisopropylphosphonium tetraphenylborate was obtained as white crystal. The yield (mol%) was 88% based on triisopropylphosphine.

[0214]

The crystal was analyzed by the methods indicated below and was identified to be triisopropylphosphonium tetraphenylborate. The analytical values and properties were as follows.

(1) Melting point: 194-214°C (decomposition temperature)

(2) IR spectrum (KBr) 2390 cm^{-1}

(3) ^{1}H-NMR spectrum (δ in DMSO-d6)

1.31 ppm (dt, 18H, J=17.4 Hz, 7.33 Hz, $(H_3C)_2$-CH-P)

2.82 ppm (dhep, 3H, J=12.3 Hz, 7.24 Hz, $(H_3C)_2$-C<u>H</u>-P)

5.93 ppm (brd, 1H, J=482.3 Hz, <u>H</u>-P)

6.79 ppm (t, 4H, J=7.15 Hz, <u>Ph</u>-B)

6.93 ppm (t, 8H, J=7.34 Hz, <u>Ph</u>-B)

7.19 ppm (brs, 8H, <u>Ph</u>-B)

(4) ^{13}C-NMR spectrum (δ in DMSO-d6)

17.2 ppm (d, J=2.5 Hz, $(H_3\underline{C})_2$-HC-P)

18.1 ppm (d, J=39.8 Hz, $(H_3C)_2$-H<u>C</u>-P)

121.4 ppm (s, <u>Ph</u>-B)

125.2 ppm (dd, J=2.3 Hz, 5.2 Hz, <u>Ph</u>-B)

135.5 ppm (d, J=1.2 Hz, <u>Ph</u>-B)

163.3 ppm (dd, J=49.1 Hz, 98.8 Hz, <u>Ph</u> quaternary-B)

The results of Examples 1 to 17 confirmed that the novel phosphonium borate compounds were produced safely, by simple reaction operations and in high yields.

[Example 18]

[0215]

Synthesis of 1-phenylheptane from n-heptyl bromide and phenylboronic acid

(Synthesis in which di-tert-butylmethylphosphonium tetraphenylborate was handled in air)

A 50-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 0.896 g (5 mmol) of n-heptyl bromide, 0.914 g (7.5 mmol) of phenylboronic acid, 0.056 g (0.25 mmol) of palladium (II) acetate, 1.683 g (15 mmol) of potassium tert-butoxide and 25 ml of tert-amyl alcohol were weighed in the flask, followed by stirring. Further, 0.240 g (0.5 mmol) of di-tert-butylmethylphosphonium tetraphenylborate obtained in Example 1 was weighed in air and added into the flask. The flask was purged with argon, followed by stirring at 25°C for 24 hours. 20 ml of saturated sodium chloride solution was added, followed by separation. The organic phase was purified by column chromatography to afford 0.785 g of 1-phenylheptane (yield: 89 mol% based on n-heptyl bromide). The identification of the product was made by mass spectroscopy.

[0216]

Mass spectrum [EI mode] M/Z 176 (M^+)

[Example 19]

[0217]

Synthesis of 4-n-heptyltoluene from n-heptyl bromide and para-tolylboronic acid

(Synthesis in which di-tert-butylmethylphosphonium tetraphenylborate was handled in air)

The procedures in Example 18 were repeated except that 0.914 g (7.5 mmol) of phenylboronic acid was replaced with 1.020 g (7.5 mmol) of para-tolylboronic acid. The organic phase was purified by column chromatography to afford 0.723 g of 4-n-heptyltoluene (yield: 76 mol% based on n-heptyl bromide). The identification of the product was made by mass spectroscopy.

[0218]

Mass spectrum [EI mode] M/Z 190 (M^+)

[Example 20]

[0219]

Synthesis of 1-phenylheptane from n-heptyl bromide and phenylboronic acid

(Synthesis in which di-tert-butylmethylphosphonium tetra-para-tolylborate was handled in air)

The procedures in Example 18 were repeated except that 0.240 g (0.5 mmol) of di-tert-butylmethylphosphonium tetraphenylborate was replaced with 0.268 g (0.5 mmol) of di-tert-butylmethylphosphonium tetra-para-tolylborate

obtained in Example 2. Consequently, 0.732 g of 1-phenylheptane was obtained (yield: 83 mol% based on n-heptyl bromide). The identification of the product was made by mass spectroscopy.

[0220]

Mass spectrum [EI mode] M/Z 176 (M^+)

[Example 21]

[0221]

Synthesis of 2-ortho-tolylpyridine from 2-chloropyridine and ortho-tolylboronic acid

(Synthesis in which tri-tert-butylphosphonium tetra-para-tolylborate was handled in air)

A 50-ml four-necked flask was equipped with a stirrer, a thermometer and a Dimroth condenser. 0.568 g (5 mmol) of 2-chloropyridine, 0.748 g (5.5 mmol) of ortho-tolylboronic acid, 0.011 g (0.05 mmol) of palladium (II) acetate, 0.959 g (17 mmol) of potassium fluoride and 10 ml of tetrahydrofuran were weighed in the flask, followed by stirring. Further, 0.029 g (0.05 mmol) of tri-tert-butylphosphonium tetra-para-tolylborate obtained in Example 3 was weighed in air and added into the flask. The flask was purged with argon, followed by stirring at 25°C for 24 hours. 10 ml of 10% aqueous sodium hydroxide solution was added, followed by separation. The organic phase was purified by column chromatography to

afford 0.677 g of 2-ortho-tolylpyridine (yield: 80 mol% based on 2-chloropyridine). The identification of the product was made by mass spectroscopy.

[0222]

Mass spectrum [EI mode] M/Z 169 (M^+)

[Comparative Example 1]

Synthesis of 1-phenylheptane from n-heptyl bromide and phenylboronic acid

(Synthesis in which di-tert-butylmethylphosphine was handled in argon)

The procedures in Example 18 were repeated except that 0.240 g (0.5 mmol) of di-tert-butylmethylphosphonium tetraphenylborate of Example 18 was replaced with 0.080 g (0.5 mmol) of di-tert-butylmethylphosphine, and except that the procedures were carried out in a glove box in which an argon atmosphere was strictly maintained. Consequently, 0.749 g of 1-phenylheptane was obtained (yield: 85 mol% based on n-heptyl bromide). The identification of the product was made by mass spectroscopy.

[0223]

Mass spectrum [EI mode] M/Z 176 (M^+)

[Comparative Example 2]

Synthesis of 1-phenylheptane from n-heptyl bromide and phenylboronic acid

(Synthesis in which di-tert-butylmethylphosphine was handled in air)

The procedures in Example 18 were repeated except that 0.240 g (0.5 mmol) of di-tert-butylmethylphosphonium tetraphenylborate of Example 18 was replaced with 0.080 g (0.5 mmol) of di-tert-butylmethylphosphine. Di-tert-butylmethylphosphine generated white smoke while being handled in air. Little 1-phenylheptane formed.

[0224]

[Comparative Example 3]

Synthesis of 2-ortho-tolylpyridine from 2-chloropyridine and ortho-tolylboronic acid

(Synthesis in which tri-tert-butylphosphine was handled in argon)

The procedures in Example 21 were repeated except that 0.026 g (0.05 mmol) of tri-tert-butylphosphonium tetra-para-tolylborate of Example 21 was replaced with 0.010 g (0.05 mmol) of tri-tert-butylphosphine, and except that the procedures were carried out in a glove box in which an argon atmosphere was strictly maintained. Consequently, 0.694 g of 2-ortho-tolylpyridine was obtained (yield: 82 mol% based on 2-chloropyridine). The identification of the product was made by mass spectroscopy.

[0225]

Mass spectrum [EI mode] M/Z 169 (M^+)

[Comparative Example 4]

Synthesis of 2-ortho-tolylpyridine from 2-chloropyridine and ortho-tolylboronic acid

(Synthesis in which tri-tert-butylphosphine was handled in air)

The procedures in Example 21 were repeated except that 0.026 g (0.05 mmol) of tri-tert-butylphosphonium tetra-para-tolylborate of Example 21 was replaced with 0.010 g (0.05 mmol) of tri-tert-butylphosphine. Tri-tert-butylphosphine generated white smoke while being handled in air. Little 2-ortho-tolylpyridine formed.

[0226]

The results of Comparative Examples 1 to 4 confirmed that the alkylphosphines could be used in combination with transition metals, salts thereof, oxides thereof or complexes thereof when the alkylphosphines were handled in an inert gas, and that the alkylphosphines were immediately oxidized in air and could not be used in combination with transition metals, salts thereof, oxides thereof or complexes thereof in air. The results of Examples 18 to 21 confirmed that the alkylphosphonium borate compounds could be used in combination with transition metals, salts thereof, oxides thereof or complexes thereof when the alkylphosphonium borate compounds

were handled in air.

[0227]

[Effects of the invention]

The invention provides the novel phosphonium borate compound. The novel phosphonium borate compound is produced by reacting the alkylphosphine hydrochloride or alkylphosphine sulfate with the tetraarylborate compound, and consequently the compound is produced safely, by simple reaction operations and in a high yield. The novel phosphonium borate compound in combination with a transition metal, salt thereof, oxide thereof or complex thereof can be used in the carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein a transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compound in combination with the transition metal, salt thereof, oxide thereof or complex thereof is used in place of the transition metal complex having a phosphine ligand.

[Document name] Abstract

[Summary]

[Means for solution]

A novel phosphonium borate compound is represented by Formula (I):

$$(R^1)(R^2)(R^3)PH\cdot BAr_4 \qquad (I)$$

wherein R^1 is a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, or a cycloalkyl group of 3 to 20 carbon atoms;

R^2 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^3 is a hydrogen atom, a primary alkyl group of 1 to 20 carbon atoms, a secondary alkyl group of 3 to 20 carbon atoms, a tertiary alkyl group of 4 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 30 carbon atoms, an aralkyl group of 7 to 20 carbon atoms, an alkenyl group of 2 to 20 carbon atoms, an alkynyl group of 2 to 20 carbon atoms, or an allyl group of 3 to 20 carbon atoms;

R^1, R^2 and R^3 may be the same or different from one another;

Ar is an aryl group of 6 to 20 carbon atoms;

R^1, R^2 and R^3 cannot be tert-butyl groups simultaneously

and Ar cannot be phenyl group at the same time; and

R^1, R^2 and R^3 cannot be cyclohexyl groups simultaneously and Ar cannot be phenyl group at the same time.

[Effects]

The invention provides the novel phosphonium borate compound. The novel phosphonium borate compound is produced by reacting an alkylphosphine hydrochloride or alkylphosphine sulfate with a tetraarylborate compound, and consequently the compound is produced safely, by simple reaction operations and in a high yield. The novel phosphonium borate compound in combination with a transition metal, salt thereof, oxide thereof or complex thereof can be used in the carbon-carbon bond forming reactions, carbon-nitrogen bond forming reactions and carbon-oxygen bond forming reactions wherein a transition metal complex having a phosphine ligand produces catalytic effects, wherein the phosphonium borate compound in combination with the transition metal, salt thereof, oxide thereof or complex thereof is used in place of the transition metal complex having a phosphine ligand.

[Representative drawing] None